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# ADVANCES IN PHYSICS

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## Electronic Band Structures of the Alkali Metals and of the Noble Metals and their $\alpha$ -Phase Alloys

By M. H. COHEN†

Cavendish Laboratory, Cambridge

and V. HEINE

Royal Society Mond Laboratory, Cambridge

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### ABSTRACT

In the monovalent metals the electronic band structure is strongly affected by the size of the band gap  $E_s - E_p$  at the Brillouin zone faces, a large gap implying a large distortion of the Fermi surface. Here  $E_s$  and  $E_p$  are the energies of the purely s-like and p-like states on the zone faces. We have made crude estimates of  $E_s - E_p$  for the alkali and noble metals, in terms of the s-p excitation energy  $\Delta_{sp}$  of the free atoms. These suggest a single model which correlates most of the experimental information about the band structures of these metals. In particular the Fermi surface of lithium appears to make considerable contact with the zone faces. In the  $\alpha$ -phase alloys of the noble metals, the solute always has a larger value of  $\Delta_{sp}$  than the solvent, which raises the energy  $E_p$  relative to  $E_s$ . The Fermi surface becomes more nearly spherical in copper alloys than in copper, since  $E_p < E_s$ , whereas it distorts further in the gold alloys ( $E_p > E_s$ ). This accounts for many Knight shift, electronic specific heat, magnetic susceptibility and other data on these alloys. Furthermore it provides the extension of Jones' explanation of the Hume-Rothery rule demanded by the non-spherical Fermi surface in pure copper and gold.

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† Guggenheim Fellow 1957-58 on leave from Institute for the Study of Metals, University of Chicago.

## § 1. INTRODUCTION

IN recent years many measurements of electronic properties of the monovalent metals have been made. The anomalous skin effect, optical constants, specific heat, Knight shift, soft x-ray emission and various transport properties all give information about the electronic structures of these metals. It is of great interest, therefore, to collate this information with a view to obtaining the form of the electronic band structure from experiment, and then to compare this with the predictions of band theory. At the present time the experimental data are rather incomplete, and we review what information exists. As we shall see, this is in general enough to describe semiquantitatively the amount that the Fermi surface is distorted from a sphere, and whether the wave functions at the Brillouin zone faces have mainly s-like or p-like character. Concerning the theoretical side, a band structure calculation is lengthy and subject to technical difficulties and considerable errors. Moreover it too often focuses attention on a single metal when what is needed is an understanding of systematic variations from metal to metal. For these reasons we are concerned here with the development of a simple, semiquantitative scheme for the band structure which embraces all the monovalent metals and serves as a basis for comparison with experiment.

Another primary concern of the present work is the interrelation of the electronic structures of the noble metals and of their  $\alpha$ -phase alloys. In 1934 Hume-Rothery, Mabbott and Chanel-Evans (1934) discovered that the maximum solid solubility of the elements of the B sub-groups in copper and silver corresponded to an electron to atom ratio ( $e/a$ ) of approximately 1.4 (Raynor 1949). Shortly afterwards Mott and Jones (1936) and, independently, Konobejewski (1936) related this remarkable regularity to the touching of the surface of the first Brillouin zone (BZ) by the Fermi sphere according to the principle enunciated by Jones (1934 a, b). Jones (1937) followed with a more quantitative treatment of the copper alloys. Apart from Friedel's (1954) important observation that the localization of the screening electrons round the solute atoms and in particular the possible presence of bound states does not, for instance, upset Jones' interpretation of the Hume-Rothery rule, the theoretical situation has remained unchanged to date.

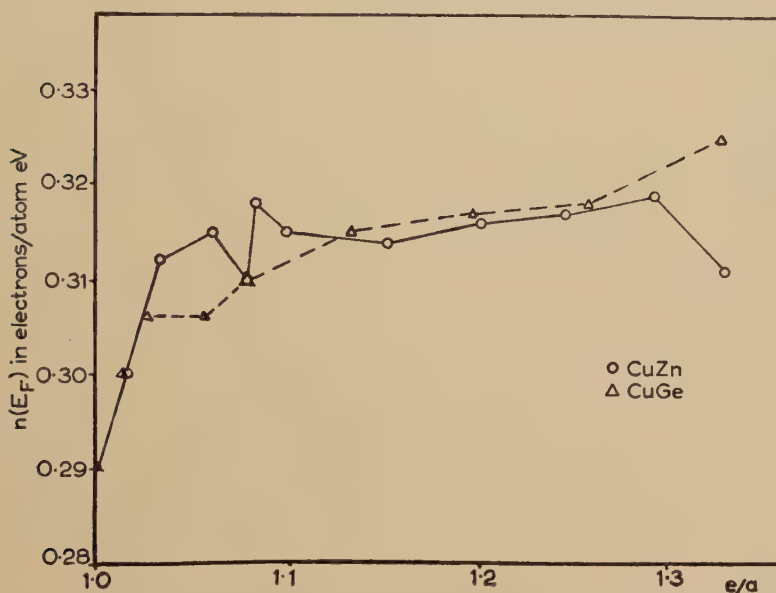
In constructing his model, Jones in effect assumed (1) the Bloch independent-electron model of a metal; (2) the applicability of band theory to alloys having a random arrangement of atoms; (3) the energy  $E(k)$  of the electrons with wave vector  $k$  is nearly spherically symmetrical except close to the zone faces, and in particular the Fermi surface (FS) is nearly spherical; and (4) the rigid band model of an alloy, i.e. the shape of the density of states,  $n(E)$ , is unaffected by alloying.

We note in particular that the Jones interpretation of the Hume-Rothery rule depends on the assumption that Cu has a nearly spherical Fermi surface and on the consequent maximum in  $n(E)$  at a value of  $e/a$  of  $\simeq 1.36$ , when the FS first touches the zone faces.



Now measurements of anomalous skin effect by Pippard (1957) have shown that the Fermi surface already contacts the zone boundary in pure copper, thus removing one of the basic props of the Jones theory. Nevertheless we reject the idea that the agreement between the Jones theory and experiment is fortuitous, in view of its notable success not only for Cu alloys but also for those of Ag and to a lesser extent Au. We are left with the question: (i) How do we reconcile the validity of the Hume-Rothery rule for the Cu alloys with the experimental results of Pippard (FS touching BZ boundaries)? Further, there is no distinction between Cu, Ag, and Au in Jones' explanation of the Hume-Rothery rule.

Fig. 1



Dependence of the density of states at the Fermi level  $n(E_F)$  on electron to atom ratio ( $e/a$ ) in CuZn and CuGe alloys as determined experimentally from the electronic specific heat (Rayne 1957 a, 1958) ( $\gamma = \frac{1}{3}\pi^2 k^2 n(E_F)$ ).

This leads to a second question: (ii) why do the phase boundaries of gold alloys occur at systematically lower values of  $e/a$  than those of copper and silver alloys? A third question concerns the measurements of Rayne (1957 a, 1958). His results for the dependence of the coefficient  $\gamma$  of the electronic specific heat on concentration in  $\alpha$ -CuZn and  $\alpha$ -CuGe are displayed in fig. 1. The initial rapid rise of  $\gamma$  suggests at first sight that the FS touches the zone face at a value of  $e/a$  of about 1.1. This suggestion is completely in line with the model of Jones if we assume that the FS in copper is somewhat distorted from the spherical (Jones 1937) but does not touch the zone faces. The third question is this (iii) How then do we reconcile Rayne's results with the contact of FS and zone faces required by the experiments of Pippard?

The difficulties thus encountered lead us to re-examine assumptions (1)–(4). Given the present development of the theory of metals and alloys, it is difficult to state conclusively that assumptions (1) and (2) are not at fault. Nevertheless, we feel that something like a fundamental justification of the independent-electron model is beginning to emerge from the work of Bohm and Pines (Pines 1955), Mott (1956), Gell-Mann and Brueckner 1957, Gell-Mann 1957, Sawada 1957, Sawada *et al.* 1957, Brout 1957. We also feel that something like a band theory of alloys is valid whenever the mean free path is much longer than the electron wave lengths involved. This view is supported by the recent results of Weiss and Abrahams (1958) and of Edwards (1958) (see also Knight and Heine 1959). Accordingly, we attempt to answer the three questions above within the conventional framework of band theory, focusing our attention entirely on the breakdown of assumptions (3) and (4). The breakdown of the former is demonstrated by Pippard's measurements. We also believe that Pippard's and Rayne's measurements, taken together, indicate the breakdown of the rigid-band model (assumption (4)) as follows. We presume that the change of slope at  $e/a \sim 1.1$  really indicates a zone boundary effect as suggested by the form of the data (fig. 1). Then the fact that the FS already touches the zone faces in pure copper (Pippard 1957) means that the effect at  $e/a \sim 1.1$  can only be a pulling away of the FS from the zone faces. This is clearly incompatible with the rigid filling up of the band structure by electrons in the rigid-band model.

Any model which attempts to describe the band structure of alloys must start out from a correct theory of the pure metals. Hence in setting out to answer our three questions above, we first find a realistic model of the band structures of the pure metals. Secondly we replace the rigid-band model by one which predicts the manner in which a band deforms on alloying.

Thus we begin in § 2 with a semiquantitative model of the band structure applicable both to the pure monovalent metals (including the alkalis as well) and to their  $\alpha$ -phase alloys which we use instead of assumption (3). Let  $E_s$  and  $E_p$  be the energies of the purely s-like and purely p-like states at the centres of the Brillouin zone faces nearest  $k=0$ . The band gap  $E_s - E_p$  is a key feature of the band structure of these substances. For example, the distortion of the Fermi surface from the spherical depends on the magnitude of  $E_s - E_p$ . Our model therefore assigns a dominant role to the magnitude and sign of  $E_s - E_p$ . It is sometimes possible to arrive at a definite sign and even an estimate of the magnitude of  $E_s - E_p$  solely from consideration of the available experimental evidence. For clarity of presentation, however, we first make crude estimates of the values of  $E_s - E_p$  for the pure metals and construct the specific model of the band structure of each metal suggested by these. We then show that with minor modifications the proposed band structures are consistent with all the directly relevant experimental evidence. We discuss in this



way the alkalis in § 3 and the noble metals in § 4. Good agreement between experiment and theory is obtained, except possibly for silver. The way our model accounts for the band structures of the pure metals is of course of interest in its own right. However, it also gives us confidence in applying the same ideas to the band structure of the noble metal  $\alpha$ -phase alloys in § 5, where we give our proposed answers to questions (i) to (iii) above and explanations of other data.

In our model of the band structure, the required estimate of  $E_s - E_p$  is made by relating it to the s-p excitation energy  $\Delta_{sp}$  in the free atom (§ 2). General trends in band structure with position in the periodic table can thus be understood in terms of the corresponding trends in  $\Delta_{sp}$  and the atomic volume, which generally increase as one moves down or to the right in the periodic table. In this way the systematic trends among the alkali metals and the noble metals can be accounted for. Also in the  $\alpha$ -phase alloys of the noble metals, the solute atom always has a larger  $\Delta_{sp}$  than the solvent atom. Whatever the details, the energy  $E_p$  must be raised relative to  $E_s$  as the concentration increases. This, we believe, is the source of the breakdown of the rigid band model (assumption (4)) for these alloys. Our model assigns  $E_p < E_s$  in pure copper. Therefore the Fermi surface becomes more nearly spherical in the copper alloys, and Jones' explanation of Hume-Rothery's rule works despite the non-spherical Fermi surface in pure copper (question (i)). Similarly the initial rise in the  $\gamma$  of  $\alpha$ -CuZn and  $\alpha$ -CuGe alloys (fig. 1) is caused by the Fermi surface first pulling away from the zone face, contact ceasing or the area of contact being a minimum at  $e/a \sim 1.1$  (question (iii)). On the other hand, the Fermi surface distorts further in the gold alloys, where  $E_s < E_p$  according to our model. Contact with the surface of the Brillouin zone must occur at low  $e/a$  and increase monotonically with concentration. We suggest that this is why the solid solubility limits of gold alloys occur at low  $e/a$  values (question (ii)). For silver, the magnitude of  $E_s - E_p$  is probably small and the Fermi surface nearly spherical. Jones' explanation of the Hume-Rothery rule goes through essentially unmodified. However, the existing experimental evidence definitely leaves uncertain the magnitude of the distortion from the spherical of the Fermi surface in silver. This and other questions of the extent to which our various models are uniquely required by the experimental results are discussed in § 6.

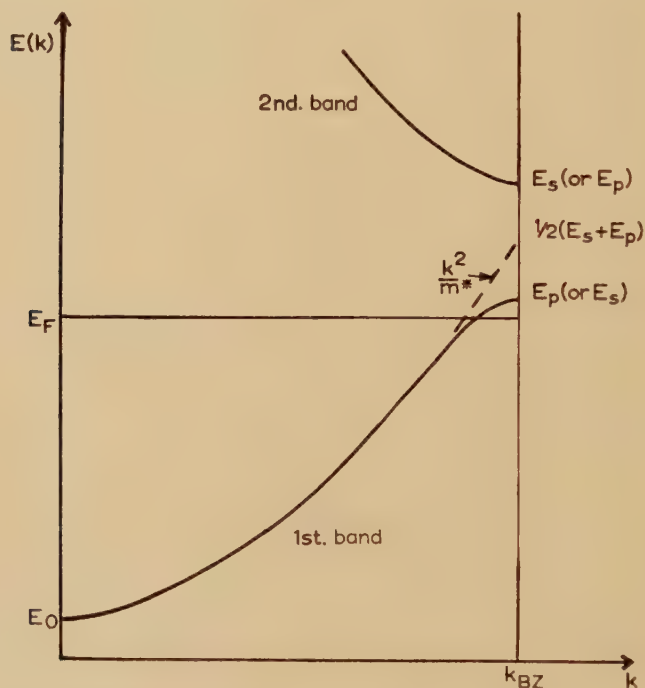
Our emphasis throughout of the importance of  $\Delta_{sp}$  in relation to the electronic properties of metals and alloys should not be surprising. The importance of  $\Delta_{sp}$  for chemical valences and structural chemistry has long been appreciated. Mott (1934) and Wigner and Seitz (1955) have already made use of relative values of  $\Delta_{sp}$  in discussions of the properties of metals. The crystal structures of the group IV elements furnish an elementary and familiar example of the power of such arguments. C, Si and Ge all crystallize in the diamond structure. These are light elements,  $\Delta_{sp}$  is small, s-p hybridization is relatively easy, and the tetrahedrally coordinated diamond structure results. For tin, however,  $\Delta_{sp}$  is larger, and

a metallic structure (white tin) differs but little in energy from the diamond structure (grey tin). Finally,  $\Delta_{sp}$  is so large for lead that hybridization is difficult, and lead crystallizes in a normal, close-packed, metallic structure.

## § 2. A MODEL OF THE BAND STRUCTURE

General experience indicates that in metals the energy gap  $E_2(\mathbf{k}) - E_1(\mathbf{k})$  at the surface of the Brillouin zone is of the order of 1 electron volt (ev), where  $E_1(\mathbf{k})$  and  $E_2(\mathbf{k})$  refer to the first and second bands respectively. The evidence for this comes from detailed band structure calculations, from the fact that divalent metals are not insulators, and other experimental facts such as the observed Fermi surface in lead (Gold 1958). In

Fig. 2



Band structure  $E(k)$  of a monovalent metal in the direction of the zone face closest to the origin.

cubic metals the next bands lie considerably higher in energy except perhaps near the zone corners, which suggests that the wave functions of the lowest band can be adequately represented as linear combinations of two orthogonalized plane waves (OPW). Further,  $E_2(\mathbf{k}) - E_1(\mathbf{k})$  is sufficiently large in the interior of the zone for the wave functions of the lowest band to be adequately represented by a single OPW.  $E_1(\mathbf{k})$  is



then spherically symmetrical, apart from the lowering associated with the proximity of a zone face (fig. 2). For a monovalent (alkali or noble) metal, therefore, the Fermi surface is a sphere of radius  $k_F$  which bulges outwards in the direction of those Brillouin zone faces closest to the centre. These are the  $\langle 111 \rangle$  and  $\langle 110 \rangle$  faces in the face-centred cubic and body-centred cubic structures, respectively, and we denote their distance from the zone centre by  $k_{BZ}$ . The amount of bulging may of course be so large that the Fermi surface actually makes contact with the zone face. We shall defer discussion of the influence on the shape of the Fermi surface of other symmetry points on the zone boundary until the end of this section.

We characterize the band structure by the three key levels  $E_0$ ,  $E_s$ ,  $E_p$  of fig. 2.  $E_0$  is the energy at  $k=0$ , and is associated with a spherically symmetrical, s-like state  $\psi_0$ . At the zone face the states are either s-like ( $E_s, \psi_s$ ) or p-like ( $E_p, \psi_p$ ) but not a mixture of both. In the interior of the zone, the  $\cos \mathbf{k} \cdot \mathbf{r}$  part of an OPW behaves as an s-like function near the nuclei and the  $\sin \mathbf{k} \cdot \mathbf{r}$  as a p-like function, so that the energy is a linear combination of s-state and p-state energies. We suppose therefore that apart from the energy splitting at the zone face the energy follows the dotted curve of fig. 2, passing through the mean of  $E_s$  and  $E_p$ . Assuming the band to be roughly parabolic away from the zone faces ( $E_1(\mathbf{k}) = k^2/m^*$  in atomic units), we have therefore for the effective mass parameter

$$\frac{1}{m^*} \simeq \frac{\frac{1}{2}(E_s + E_p) - E_0}{k_{BZ}^2} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and for the Fermi level  $E_F$

$$E_F - E_0 \simeq k_F^2/m^* \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For both the f.c.c. and the b.c.c. structures we can put

$$k_F^2 \simeq 4/5 k_{BZ}^2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The distortion of the Fermi surface depends on the amount  $\frac{1}{2}|E_s - E_p|$  that the energy at the zone face is depressed below the mean parabolic form (fig. 2), and we shall use as a measure of the distortion the parameter

$$d = \frac{\frac{1}{2}(E_s - E_p)}{\frac{1}{2}(E_s + E_p) - E_F} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

When  $|d| \geq 1$ , it means that either  $E_s$  or  $E_p$  is depressed below the Fermi level  $E_F$  so that the Fermi surface bulges outwards enough to touch the zone faces.

We now express the energies  $E_0$ ,  $E_s$ ,  $E_p$  approximately in terms of the atomic levels  $\epsilon_s$ ,  $\epsilon_p$  in the spirit of the quantum defect method of calculating band structures (Ham 1955). We put

$$E_0 = \epsilon_s - (BC)_s \quad \text{and} \quad E_p = \epsilon_p - (BC)_p, \quad . \quad . \quad . \quad . \quad (5)$$

which defines the boundary corrections BC. The name boundary

correction refers to the fact that the Schrödinger equation requires different boundary conditions in the atom and in the solid. For the atomic case we require  $\psi \rightarrow 0$  at infinity, whereas for  $\psi_0$  and approximately for  $\psi_p$  we require  $\partial\psi/\partial r = 0$  on the boundary of the atomic cell so as to make the parts of the wave function in consecutive cells join smoothly. As regards the magnitude of  $(BC)_s$  and  $(BC)_p$ , we note that the p-state is less tightly bound than the s-state. This and more detailed considerations suggest that  $(BC)_p$  is smaller than  $(BC)_s$ , and we arbitrarily and very crudely suppose that

$$(BC)_p \sim \frac{1}{2}(BC)_s. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In the limit of small ion cores,  $\psi_s$  has the same shape as  $\psi_0$  near the atomic nuclei, but has an extra node in the plane wave part between the nuclei. This introduces extra kinetic energy about equal to  $k_{BZ}^2$ , or <sup>(1)†</sup>

$$E_s \simeq E_0 + k_{BZ}^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

From eqns. (1) to (7), we now obtain the approximate results

$$E_s - E_p = -\Delta_{sp} - [(BC)_s - (BC)_p] + \frac{5}{4}k_F^2 \quad . \quad . \quad . \quad . \quad (8a)$$

$$\simeq -\Delta_{sp} - \frac{1}{2}(BC)_s + \frac{5}{4}k_F^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (8b)$$

$$d = \frac{(E_s - E_p)}{\frac{1}{2}k_F^2 - \frac{1}{5}(E_s - E_p)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$m^* = 1 + d/5. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

We evaluate these quantities from the three parameters involved:  $k_F^2$  which is determined by the atomic volume,  $\Delta_{sp}$  which is derived from the observed atomic term values (table 1), and  $(BC)_s$  which is known from previous band structure calculations. We obtain from the magnitude of  $d$  the amount of distortion of the Fermi surface, from the sign of  $d$  whether the s-like or p-like level lies lowest, and from  $m^*$  the trend of the effective mass. The quantity  $d$  thus plays the central role in our description of the band structures of monovalent metals and their  $\alpha$ -phase alloys. Moreover,  $d$  depends on  $\Delta_{sp}$  so that systematic changes in the atomic quantity  $\Delta_{sp}$  are immediately reflected in the band structure through the corresponding changes in  $d$ . This semi-quantitative relation of the band structure to the atomic s-p excitation energy is the novel and the most important feature of our model.

A large atomic volume, i.e. small  $k_F^2$ , and a large  $\Delta_{sp}$ , often associated with high atomic number (see table 1), both favour a small value of  $E_s - E_p$ . Thus  $E_s - E_p$  decreases steadily from Li to Cs in the alkalis, table 2, since both the atomic volume and atomic number are increasing, and the same tendency is seen in the series Cu, Ag, Au, table 2. (Typical values of the quantities  $\frac{5}{4}k_F^2$ ,  $\frac{1}{2}(BC)_s$ , and  $\Delta_{sp}$  used in calculating the  $E_s - E_p$  of table 2 are 3.95, 1.58 and 2.10 eV for Na and 8.87, 3.65 and 3.81 eV for Cu.)

† Numerical superscripts refer to notes added in proof at the end of the text.



Table 1. Values of  $\Delta_{sp}$ (ev)

atom $\Delta_{sp}$	Li 1.85	Na 2.10	K 1.61	Rb 1.58	Cs 1.44
atom $\Delta_{sp}$	Cu 3.81	Zn 5.78	Ga 7.9	Ge 6.6	As 6.7
atom $\Delta_{sp}$	Ag 3.75	Cd 5.29	In 7.5	Sn 5.6	Sb 6
atom $\Delta_{sp}$	Au 4.75	Hg 6.70	Al 6.9	— —	— —

The values of  $\Delta_{sp}$  have been deduced from the atomic term values as tabulated by Moore (1949, 1952) and Landolt-Börnstein (1950). The  $\Delta_{sp}$  for the polyvalent elements are open to considerable error. This is partly due to the paucity or even non-existence of the required term values, in which case we have resorted to extrapolation from neighbouring elements and from the term values of the various degrees of ionization. When the term values are known, the difficulty is that the configurations  $s^2p^x$  and  $sp^{x+1}$  both have several terms differing considerably in energy. We have compared terms with the same  $S$  and when possible with angular momentum  $L$  and  $L+1$  respectively so as to minimize the difference in exchange and correlation energy between the two terms. Finally, we have averaged over different pairs of terms if possible.

Table 2. Comparison of  $E_s - E_p$ 

Metal	$E_s - E_p$ from (8) (ev)	$E_s - E_p$ band structure calculations (ev)	References
Li	2.08	3.03	G and C
—	—	2.57	S
—	—	small	K and R, and P
Na	0.27	-0.65	H and J
K	-0.12	-0.46	C
Rb	-0.35	—	—
Cs	-0.44	0.76	C and H
Cu	1.4	-1.42, -1.92, -0.27, -1.70 }	H
Ag	0.1	—	—
Au	-0.8	—	—

References: G and C=Glasser and Callaway (1958), S=Schiff (1954), K and R=Kohn and Rostoker (1954), P=Parmenter (1952), H and J=Howarth and Jones (1952), C=Callaway (1956), C and H=Callaway and Haase (1957), H=Howarth (1953 and 1955, various potentials and calculations).

The results of detailed band structure calculations of  $E_s - E_p$ , as displayed in table 2, do not show this simple trend with atomic number. Moreover, the detailed calculations are subject to various errors, among which is a systematic tendency to *underestimate*  $E_s - E_p$  (Appendix A). For these reasons and despite the crudeness of eqn. (6), we prefer our values of  $E_s - E_p$  as a basis for comparing our scheme for the band structure with experiment. In fact, the comparison with experiment carried out in §§ 3, 4 and 5 shows our values of  $d$ , and hence of  $E_s - E_p$ , to be better than is expected from the crudeness of our approximations.

It is of interest to explore how our description of the band structure depends on the atomic volume or the lattice constant  $a$ . Let us take the very crudest approximation to the cohesive energy  $U$ ,

$$U \sim E_0 + \frac{3}{5} E_F \sim E_s - (BC)_s + \frac{3}{5} k_F^2 / m^*. \quad . \quad . \quad . \quad (11)$$

Imposing the equilibrium condition  $dU/da = 0$  on (11) gives us

$$\frac{d}{da} (BC)_s \sim \frac{3}{5} \frac{d}{da} \frac{k_F^2}{m^*}. \quad . \quad . \quad . \quad (12)$$

From (12), (8*b*) and the proportionality of  $k_F$  to  $1/a$ , we see that  $E_s$  increases relative to  $E_p$  when the volume decreases,

$$\frac{d}{da} (E_s - E_p) < 0. \quad . \quad . \quad . \quad (13)$$

This is the required result, and detailed considerations suggest that the validity of (13) remains unaffected by the  $d$ -shells in the case of the noble metals.

So far we have considered only the effect of the energy at the centres of the nearest zone faces on the shape of the Fermi surface, which raises the question of whether other points on the zone boundary can have a comparable effect. The approximation (6) is clearly too rough since it gives all p-like states on the zone boundary the same energy. If this were so and at the same time  $E_p < E_s$ , then the Fermi surface would bulge most in the direction of the zone corners farthest from the centre. However, detailed calculations by Callaway and others (see references of table 2) and the explicit equations of the OPW approximation show that the energy of the p-state on the zone surface in general increases with the distance from the centre. Thus a bulging of the Fermi surface towards the nearest zone faces is the most likely type of distortion to occur, and we shall restrict our discussion to this type of shape.

### § 3. THE ALKALI METALS

We consider first the alkali metals. The values of  $d$  and  $m^*$  calculated from (9) and (10) are shown in table 3. We note that our values of  $m^*$  show the same trend as the values estimated for the individual metals by the quantum defect method (line 3, table 3), and the values determined from the observed electronic species heat (line 4) although the latter are not



really direct measures of  $m^*$ . The signs of  $d$  indicate that at the centre of the nearest zone face p-like levels are lowest for Li and Na and s-like levels are lowest for K, Rb, and Cs. The magnitudes of  $d$  indicate that the Fermi surface is relatively undistorted in Na and K, appreciably distorted in Rb, and still more distorted in Cs. For Li, the value of  $d$  is greater than unity, and the Fermi surface actually makes contact with the nearest zone faces.

On this model for Li the density of states  $n(E)$  rises sharply to a maximum at the energy  $E_p$  at the centre of the zone face, and then drops to a lower value at the Fermi level  $E_F$ . We propose that this is the explanation of the shape of the observed *soft X-ray (K) emission spectrum* of lithium, which exhibits

Table 3. Properties of the Alkali Metals

	Li	Na	K	Rb	Cs
1. $d$ from (9)	1.06	0.18	-0.11	-0.36	-0.5
2. $m^* = 1 + d/5$ from (10)	1.22	1.03	0.98	0.93	0.90
3. $m^*$ calc. from QDM	1.38	0.98	0.94	0.91	0.83
4. $m^*$ obs. from sp. ht.	2.3	1.22	1.1	—	—
5. $m^*$ obs. from soft x-ray emission	$\sim 1.2$	$\sim 1$	$\sim 1$	—	—
6. $\xi$ obs. (Knight shift)	0.43	0.72	—	1.0	1.3

Notes: The values of  $\Delta_{sp}$  and  $(BC)_s$  required to calculate lines 1 and 2 were taken from Moore (1949, 1952) and Landolt-Börnstein (1950), and Ham (1955), respectively. The values of  $m^*$  in line 3 have been taken from the quantum defect method (QDM) calculation by Brooks (Ham 1955). In lines 4 and 5 the comparison should ideally be with some average effective mass for the whole band. In the absence of any such accurate data, we show the masses determined from the electronic specific heat (Roberts 1957) and soft x-ray emission spectrum (for data see text). The values of  $\xi$  are from Knight (1956).

just such an effect (Bedo and Tombouliau 1958, Catterall 1957). Moreover, the positive  $d$  indicates that the occupied states at the zone face are purely p-like. This tends to accentuate the maximum because for an arbitrary  $\mathbf{k}$  it is only the p-part of  $\psi_{\mathbf{k}}$  that enters into the transition matrix element. Mott (1953) has given an alternative explanation of the soft x-ray emission spectrum in terms of a model with  $E_s < E_p$ , but we find this very improbable in view of our large estimate of  $E_s - E_p \sim +2.1$  ev from (8b), and of Glasser and Callaway's calculated result of  $E_s - E_p = +3.03$  ev (table 2). The  $L_3$  emission spectrum of Na and the  $M_3$  emission spectrum of K, on the other hand, are consistent with spherical Fermi surfaces for both metals (Tombouliau 1957). The reduced band widths are 3.2 ev for Li (Bedo and

Tomboulian 1958),  $3.0 \pm 0.2$  eV for Na and  $1.9 \pm 0.2$  eV for K (Tomboulian 1957). The ensuing values of  $m^*$  are  $\sim 1.2$  for Li and  $\sim 1$  for Na and K (table 3).

A second property which is sensitive to the order of the levels  $E_s$  and  $E_p$  is the *Knight shift* (nuclear magnetic resonance shift), to which only the s-like parts of the occupied states  $\psi_k$  contribute. The experimental results are often expressed in terms of a factor  $\xi$  which is interpreted as the proportion of atomic s-like character in the  $\psi_k$  averaged over the Fermi surface (Knight 1956). Thus  $\xi$  will tend to be small when  $E_p$  lies below  $E_s$  and large when  $E_s < E_p$ . The greater the magnitude of  $d$ , i.e. the greater the proximity of  $E_s$  or  $E_p$  to the Fermi level, the greater is the effect. The observed  $\xi$ 's do indeed show this expected correlation. Benedek and Kushida (1958) have reported the volume dependence of the Knight shift for Li, Na, Rb, and Cs. The Knight shift is proportional to  $n(E_F)\xi$  [see eqn. (21) where  $\chi$  is proportional to  $n(E_F)$ ]. Aside from distortions of the FS, the Knight shift should increase with pressure because both  $n(E_F)$  and  $\xi$  increase with the increasing electron density, and this is observed in Na, Rb, Cs. In Li we attribute the observed small decrease with pressure to the increase in  $E_s - E_p$  (eqn. 13), which lowers  $n(E_F)$  due to the distortion of the FS and which increases the proportion of p-character<sup>(2)</sup> in the  $\psi_k$ .

It is difficult to obtain clear evidence about the shape of the Fermi surface from *transport properties*. Those effects such as the anomalous skin effect, cyclotron resonance, and the infra-red optical constants which relate directly to the shape of the Fermi surface have not yet been measured. All other properties depend explicitly on the complicated scattering mechanisms, so that we shall only be able to extract information about the band structure in a qualitative way. From table 3, the distortion of the Fermi surface in sodium and potassium should be small, in agreement with the general experience that of all metals these two seem to be closest to the free electron model. The values of  $d$  for rubidium and caesium are rather larger ( $-0.36$  and  $-0.51$ ) and suggest a greater distortion of the Fermi surface, as proposed already by Klemens (1954a, b, 1956, p. 238ff.) on the basis of thermal and electrical conductivity data. The extreme distortion of the Fermi surface suggested by us for lithium may well open the possibility of understanding its various anomalous transport properties. We shall now consider a number of transport effects in detail.

Klemens (1954a, b, 1956, p. 198) has pointed out that the ratio of the *low temperature electrical and thermal resistivities* is sensitive to the shape of the Fermi surface. As discussed in Appendix B, the quantity

$$D = \frac{64.0}{497.6} \frac{\Theta_p^6}{\Theta_p^4} \frac{\rho_i(T)}{L W_i(T) T^3} \quad \dots \quad (14)$$

should exceed unity for a spherical Fermi surface and should increase with the distortion of the Fermi surface. In eqn. (14),  $\rho_i(T)$  is the ideal electrical and  $W_i(T)$  the ideal thermal resistivity in the temperature range where they are proportional to  $T^5$  and  $T^2$ , respectively;  $\Theta_p$  and  $\Theta_{pr}$  are the respective

characteristic temperatures which in principle differ:  $L$  is the Lorentz number; and the numerical factor derives from Klemens' (1954c) solution of the Bloch integral equation (Sommerfeld and Bethe 1933, p. 517ff.). Because of the uncertainty in  $\Theta_\rho$  and  $\Theta_W$ , we obtain  $D$  by first calculating the quantity  $D'$  considered by Klemens

$$D' = \frac{64 \cdot 0}{497 \cdot 6} \frac{\Theta_D^2}{L} \frac{\rho_i(T)}{W_i(T)} \quad \dots \quad (15)$$

which depends only on measured quantities, and then estimating the ratio

$$D'/D = \Theta_W^4 \Theta_D^2 / \Theta_\rho^6 \quad \dots \quad (16)$$

For all the metals for which the data required for estimating  $D'/D$  exist,  $D'/D$  turns out to be near unity (Appendix B). In the cases where these data do not exist, we may therefore use  $D'$  as a rough measure of  $D$ . Values of  $D'$ , and where possible  $D$ , are entered in table 4. There is indeed a pronounced correlation between  $D'$  (or  $D$ ) and  $d$ , confirming our picture once more.

Table 4. Values of  $D'$  and  $D$  for the Alkali Metals

Metal	Li	Na	K	Rb	Cs
$D'$	19.3	3.1	6.8	14.2	15.7
$D$	—	2.8	4.3	—	—
$d$	1.06	0.18	-0.11	-0.36	-0.51

Notes:  $D'$  was calculated from eqn. (15). Values for  $\rho_i/W_i T^3$  were taken from MacDonald *et al.* (1956). Values of  $\Theta_D$  for Li, Na and K were taken from Roberts (1957) and for Rb and Cs from Dauphinee *et al.* (1955).  $D$  was calculated from eqn. (14) by using the tabulated values of  $D'$  and the estimates of  $D'/D$  (eqn. (16)) obtained in Appendix B.

Moliner (1958) has studied the *galvano-magnetic properties* of the alkali metals in some detail. His conclusions concerning the relative anisotropies of the Fermi surface are in substantial agreement with our own. In particular, he has considered the metals Li, Na and K quantitatively, and finds Li to be the most anisotropic and Na to have a nearly spherical Fermi surface.

The negative signs and the magnitudes of the *thermoelectric powers*  $S$  of Na, K, Rb and Cs (Seitz 1940, p. 180) are what one expects according to Jones' calculations (1956, p. 276) based on the assumption  $E \propto k^2$  for the energy. For Li, however,  $S$  is positive, implying that the conductivity defined as a function of the energy,  $\sigma(E)$  (Jones 1956, and eqn. (18) below) decreases with increasing energy. One would expect this on physical grounds if the Fermi surface of Li is already in contact with the zone faces. The area of contact would increase with increasing energy, thus decreasing the "effective number of free electrons" (Mott and Jones, 1936, p. 97). The coupling to the lattice vibrations would also increase, particularly through Umklapp processes (see eqn. (17') below).<sup>(3)</sup>



One ordinarily expects that *pressure* increases the *electrical conductivity* of a metal by reducing the amplitude of the lattice vibrations (Mott and Jones 1936, p. 272). The conductivity of Li decreases instead. We may write the conductivity  $\sigma$  as (see eqn. (19))

$$\sigma \propto A v \tau \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where  $A$  is the area of the Fermi surface,  $v$  the average velocity at the FS, and  $\tau$  an appropriately averaged relaxation time. If the Fermi surface of Li touches the zone faces, the area of contact increases with pressure, according to eqn. (13). Whatever happens to  $\tau$ ,  $S$  and  $v$  tend to decrease with increasing area of contact when the latter is initially large enough. Further, Umklapp processes are enhanced as the area of contact increases thus opposing the increase of  $\tau$  with pressure. We suggest therefore that the negative pressure coefficient of  $\sigma$  for Li can be accounted for by the touching of the zone faces by the Fermi surface.

To sum up, the experimental evidence indicates that the Fermi surface of Na is nearly isotropic, that of K somewhat distorted, that of Rb and Cs rather more so, and that of Li actually in considerable contact with the zone boundary. Comparing these experimental conclusions with our estimates of  $d$  (table 3), we note that our value of  $|d|$  for K is too small relative to that for Na and that  $d$  for Li is even larger than our estimate. The sign of  $d$  appears to be correctly given except for uncertainty in Na where  $d \sim 0^{(4)}$ .

We conclude therefore that our scheme is in qualitative agreement with all that is known from experiment and calculation about the band structures of the alkali metals. In particular, the generally anomalous behaviour of lithium arises from a very distorted Fermi surface, which is due to the p-like level  $E_p$  having an unusually low energy. This results from a low  $\Delta_{sp}$  and a small atomic volume (large  $k_F$ ), since from (8b) both of these effects lower  $E_p$  relative to  $E_s$ . The lithium atom is unique in having a small (1s)<sup>2</sup> ion core instead of the usual (ns)<sup>2</sup>(np)<sup>6</sup> configuration. The smallness of the core results in the valence electron not being pushed out so far by the exclusion principle, giving the small atomic volume. The potential is also closely hydrogenic because of the small core, which explains why  $\Delta_{sp}$  is small ( $\Delta_{sp}=0$  for a pure  $1/r$  potential). The anomalous properties of lithium metal are therefore seen to be a direct consequence of its unique position in the periodic table.

#### § 4. THE NOBLE METALS

The values of  $d$ ,  $m^*$  and  $E_s - E_p$  have been calculated for the noble metals from (9), (10) and (8b), and are shown in table 5. The values of  $d$  indicate that in gold the s-like level  $E_s$  at the zone face is lowest, and that the distortion of the Fermi surface is considerable but not so large that the Fermi surface touches the zone faces. In silver we predict that  $E_s$  and  $E_p$  have nearly the same energy, with  $E_p$  probably lying below  $E_s$ , resulting in a nearly spherical Fermi surface. In copper the value of  $d$  predicts a large distortion of the Fermi surface, with  $E_p$  lying below  $E_s$ . Table 5 shows

also the values of  $m^*$  obtained from the quantum defect method of calculating band structures. Our estimates from (10) are seen to be in accordance with these as regards general trend.

As mentioned in § 3, there are two properties which are sensitive to s-like or p-like nature of  $\psi_k$ , and thus to the order of the levels  $E_s$  and  $E_p$ . Firstly, Mott (1953) has already interpreted the x-ray spectrum of copper as suggesting that  $E_p$  lies below  $E_s$  in agreement with our calculation (table 5). Secondly, we have for the observed Knight shift factor  $\xi$  introduced in § 3 that  $\xi_{\text{Cu}} = 0.53$  is less than  $\xi_{\text{Ag}} = 0.70$ . This is immediately explained in terms of our model by the difference in  $d$  between copper and silver (table 5), in accordance with the reasoning of § 3. Somewhat more conclusive evidence for the fact that the occupied states in copper at the zone faces have p-like symmetry comes from the Knight shift data on alloys to be considered in § 4.

Table 5. Band Structure Parameters for the Noble Metals

	Cu	Ag	Au
1. $d$ from (9)	0.40	0.04	-0.27
2. $E_s - E_p$ from (8) eV	1.42	0.10	-0.75
3. $m^*$ from (10)	1.08	1.01	0.95
4. $m^*$ from QDM	1.013	0.993	0.990
5. $m_0$ from optical constants	1.45	0.97	0.98

These estimates are based on  $\Delta_{\text{sp}}$  taken from Moore (1949, 1952) and Landolt-Börnstein (1950), and on  $(\text{BC})_s$  taken from Kambe (1955). The values of  $m^*$  in line 4 have been calculated by Kambe (1955) using the quantum defect method. Values of  $m_0$  are taken from Schulz (1957) and Cohen (1958).

Pippard's analysis of the *anomalous skin effect* data for Cu (Pippard 1957) leads him to propose a Fermi surface in contact with the zone boundary. In doing so, he asserts that if contact does not occur then the Fermi surface must run extremely close to the boundary. Direct information about the distortion of the Fermi surface is also obtainable from a comparison of the *optical constants* in the infra-red with the *electronic specific heat* (Cohen 1958). The result of this comparison for Cu rules out a Fermi surface which very nearly touches the zone boundary and favours Pippard's proposal of contact. Therefore, our value of  $d$  for Cu (table 5) is a considerable underestimate; contact occurs and  $d > 1$  for Cu. The optical constants and electronic heat of gold indicate considerable distortion of the Fermi surface but little, if any, contact. For silver, the data are consistent both with a nearly spherical Fermi surface and with a surface making some contact. The low value of  $d$  for Ag (table 5) definitely favours the first model. Values of  $m_0$  obtained from the optical constants (Schulz 1957) are listed in table 5,  $1/m_0$  being the average inverse effective mass for the occupied states of the band (Cohen 1958). If a value of  $d > 1$  is taken for Cu, then  $m^*$  ( $= 1 + d/5$ ) becomes  $> 1.2$  in better agreement with the experimental value of 1.45 for  $m_0^{(5,6)}$ . Similarly, the experimental value of 0.97 for the  $m_0$  of Ag suggests a small value of  $|d|$  rather than the  $|d| > 1$  required for contact. The

experimental error of  $\pm 4\%$  in  $m_0$  becomes an uncertainty of  $\pm 200\%$  in  $d$  (eqn. (10)) and prevents the inference that the  $d$ 's of Ag and Au are nearly equal because the  $m_0$ 's are.

It is now possible to understand the decrease of the *Knight shift* in Cu with pressure reported by Benedek and Kushida (1958). The explanation is the same as that given for Li in § 3 in terms of  $E_p < E_s$ , contact with the zone faces, and eqn. (13).

The low field *Hall coefficient*  $A_H$  has the free electron value  $-1/Nec$  only if the Fermi surface is spherical and the scattering is elastic and isotropic in the sense that the transition probability depends only on the scattering angle. Scattering by isolated impurities is elastic and can be presumed isotropic in this sense when the Fermi surface is spherical. Therefore values of  $-A_H \times Nec$  of pure, well-annealed specimens at low temperatures give a direct measure of the anisotropy of the Fermi surface. Chambers (1956) has measured the Hall effect in polycrystalline Cu, Ag and Au at  $4^\circ\text{K}$  but found the Hall coefficient to be field dependent. A somewhat uncertain extrapolation of his data to zero field yields the values of  $-A_H \times Nec$  shown in table 6. As expected, the deviation from unity is least for Ag.

Table 6. Transport Properties of the Noble Metals

Metal	Cu	Ag	Au
1. $-A_H Nec$	0.74	1.09	0.69
2. $b'(Nec)^2$	1.3	1.9	4
3. $c'(Nec)^2$	-1.4	-1.9	-3
4. $d'(Nec)^2$	1.9	3.8	5
5. $D'$	6.4	4.4	4.3
6. $D$	6.0	3.7	3.1

Values of  $A_H$  are taken from Chambers (1956). Values of  $b'$ ,  $c'$  and  $d'$  are taken from Olson and Rodriguez (1957). The values of  $D'$  are essentially the same as those given by Klemens (1956) except that we have used the measurements of Corak *et al.* (1955) for  $\Theta_D$ . We obtain  $D$  from  $D'$  (line 5) and the values of  $D'/D$  in table 8 (Appendix B).

From the calculations of Olson and Rodriguez (1957) one can deduce that if the relaxation time is isotropic, the distortions of the Fermi surface considered by them reduce  $-A_H Nec$  below unity. A simple geometric argument yields the same result for the distortions envisaged in our model. The values of  $-A_H Nec$  for Cu and Au are indeed less than unity (table 6). For Ag,  $-A_H Nec$  exceeds unity; this and the calculations of Davis (1939) suggest that anisotropy of the scattering may play a significant role in the galvanomagnetic properties of Ag at  $4^\circ\text{K}$ . Further, the Hall coefficient of Ag depends on magnetic field in a qualitatively different manner than that of Cu or Au (Chambers 1956).



The *magnetoresistance coefficients*  $b'$ ,  $c'$  and  $d'$  of single crystals of the noble metals have been measured at 4.2°K and 20.4°K by Olson and Rodriguez (1957). These would vanish if the Fermi surfaces and scattering were both isotropic. The products of  $b'$ ,  $c'$  and  $d'$  with  $(Nec)^2$  shown in table 6 are direct measures of anisotropy for Cu, Ag and Au. They are of order unity, whereas a comparable quantity for Na would be of order  $10^{-3}$  (Jan 1958, p. 31). Olson and Rodriguez have shown that the values of  $b'$ ,  $c'$  and  $d'$  for Cu suggest contact of the Fermi surface with the nearest zone faces, but they have not interpreted their results for Ag and Au. The values of  $b'(Nec)^2$ , etc. of table 6 suggest that the relative anisotropies are in the reverse order to that proposed by us on the basis of our values of  $d$ . This difficulty is a real one; but inasmuch as most of the other experimental evidence appears to support our proposals, we suspect that the fault lies with present theories of the magnetoresistance and in particular with the simplifying assumptions that are usually made about the scattering mechanisms.<sup>(7)</sup>

The experimental situation regarding the *electrical and thermal resistivities at low temperatures* is less satisfactory for the noble metals than for the alkali metals. This is particularly so for Ag and Au where various measurements of  $W_i(T)/T^2$  differ by  $\sim 50\%$  and  $\rho_i(T)/T^5$  has not been measured on the same material as  $W_i(T)/T^2$ . Accordingly, the values of  $D'$  listed in table 6 are just taken from Klemens (1956) except that we have used more recent values of  $\Theta_D$  (Corak *et al.* 1955). We have estimated the values of  $D$  in table 6 from these values of  $D'$  and the estimate of  $D'/D$  computed in Appendix B. As discussed there and in § 3,  $D$  increases monotonically with the distortion of the Fermi surface. From the values of  $D$ , it appears that the Fermi surface of Cu is considerably more distorted than those of Ag and Au. It also appears that there is more distortion in Ag than in Au, but the conclusion is less secure because of uncertainties in the data and in the estimates of  $D'/D$ .

The *thermoelectric power* is given by the formula

$$S = -\frac{\pi^2 k^2 T}{3e} \left[ \frac{\partial (\log \sigma(E))}{\partial E} \right]_{E_F} \quad \dots \quad (18)$$

at *high temperatures* (Mott and Jones 1936, p. 310). Here  $\sigma(E)$  is the conductivity defined as a function of energy

$$\sigma(E) = \frac{e^2}{3\hbar} \frac{1}{4\pi^3} \int v\tau(\mathbf{k}) dA \quad \dots \quad (19)$$

where  $v$  is the electron velocity and  $\tau(\mathbf{k})$  the relaxation time at a point  $\mathbf{k}$  on a surface of constant energy  $E$  in  $k$ -space. Thus, we can write

$$\sigma(E) \propto Av_E \tau_E, \quad \dots \quad (17')$$

where  $v_E$  is the average electron velocity on the surface and  $\tau_E$  an appropriately averaged relaxation time. The quantity  $Av_E$  is proportional to the 'effective number of free electrons' contained within  $A$  (Mott and



both by changes in  $\Delta_{sp}$  and in  $(BC)_s$  and  $(BC)_p$  of eqn. (8a). However  $(BC)$  tends to be large when the binding energy of the level is large, so that  $(BC)_s - (BC)_p$  will be large when  $\Delta_{sp}$  is large. Hence from (8a) the changes in  $\Delta_{sp}$  and  $(BC)_s - (BC)_p$  both affect the band structure in the same direction. It is therefore sufficient to correlate the qualitative trends with  $\Delta_{sp}$  alone. Before doing so, however, we consider the information about the band structures of the pure metals derivable from Knight shift data on dilute alloys.

When a magnetic field is applied to an alloy, the net alignment of the electron spins parallel to the field is described by the bulk spin susceptibility per gram atom  $\chi$ . This spin polarization is not quite uniformly spread out in space, and we suppose as is usual in the theory of the Knight shift that at any given nucleus it is

$$\xi |\psi_A(0)|^2 \chi H / L\beta. \quad (21)$$

Here  $\psi_A(\mathbf{r})$  is the wave function of an atomic s-electron,  $L$  is Loschmidt's number, and  $\beta$  the Bohr magneton.  $\xi$  is a numerical factor which varies from atom to atom in the alloy. The utility of using this  $\xi$  factor lies in the following experimental result. In an alloy XY, the value of  $\xi$  is certainly different for X atoms and Y atoms, but appears to be remarkably constant for all X atoms (and Y atoms) independent of their surroundings. The evidence for this is that the nuclear magnetic resonance line width is considerably less than the magnitude of the Knight shift, i.e. shows relatively little 'inhomogeneous' broadening attributable to variation of  $\xi$  (Drain 1957, Rowland, private communication). Considering the *Knight shift* in the two series of dilute alloys, pure Cu, AgCu, AuCu and CuAl, AgAl, AuAl, we calculate from the data given by Knight (1956),

$$\left. \begin{array}{lll} \xi(\text{Cu in Cu}) = 0.5, & \xi(\text{Cu in Ag}) = 1.1, & \xi(\text{Cu in Au}) = 1.5; \\ \xi(\text{Al in Cu}) = 1.1, & \xi(\text{Al in Ag}) = 3.3, & \xi(\text{Al in Au}) = 5.1. \end{array} \right\} \quad (22)$$

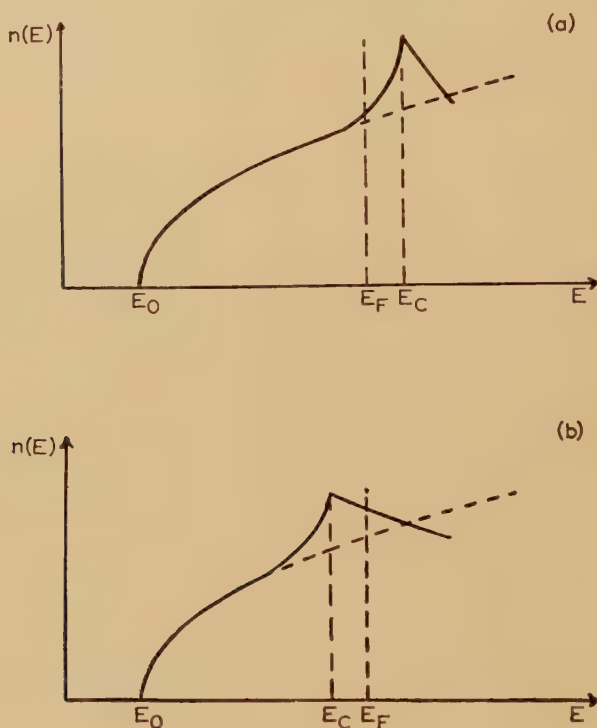
These figures have been obtained from eqn. (2.01) of Knight (1956) by assuming as a first approximation that  $\chi$  in the alloy is the same as in the pure solvent metal. The value of  $\chi$  was taken from column 4 of Knight's table II, derived from the measured electronic specific heat by the usual formula (Knight's eqn. (5.2)). However this formula is only correct in the independent particle model of the electron gas when exchange and correlation are neglected. The effect of the latter would be to reduce all the quoted values of  $\xi$  by approximately a factor of two or less without altering the ratios between them very much. The increase of  $\xi$  in (22) as we go from copper to gold affords further evidence for the view that in copper  $E_s > E_p$ , with the  $\psi_k$  at the Fermi level having predominantly p-like character, while in gold the reverse is true.

We turn now to the variation of the band structure of the alloy with solute concentration. We consider only the alloys in which the solute and solvent atoms have nearly the same size, so as to avoid complications due to lattice strain,



In the pure metal or alloy, the density of states  $n(E)$  has three characteristic features (fig. 3). First, we have  $E = E_0 + k^2/m^*$  and  $n(E) \propto E^{1/2}$  at low energies. Secondly,  $dn(E)/dE$  becomes proportional to  $(E_c - E)^{-1/2}$  as  $E$  approaches the energy  $E_c$  at which contact occurs,  $E_c = E_p$  or  $E_s$ , so that the slope of  $n(E)$  is infinite at contact. The saddle point in  $E(\mathbf{k})$  at the point of contact is what causes this vertical slope (Van Hove 1953). Finally,  $n(E)$  decreases when  $E$  exceeds  $E_c$  because of the increasing area of contact.

Fig. 3

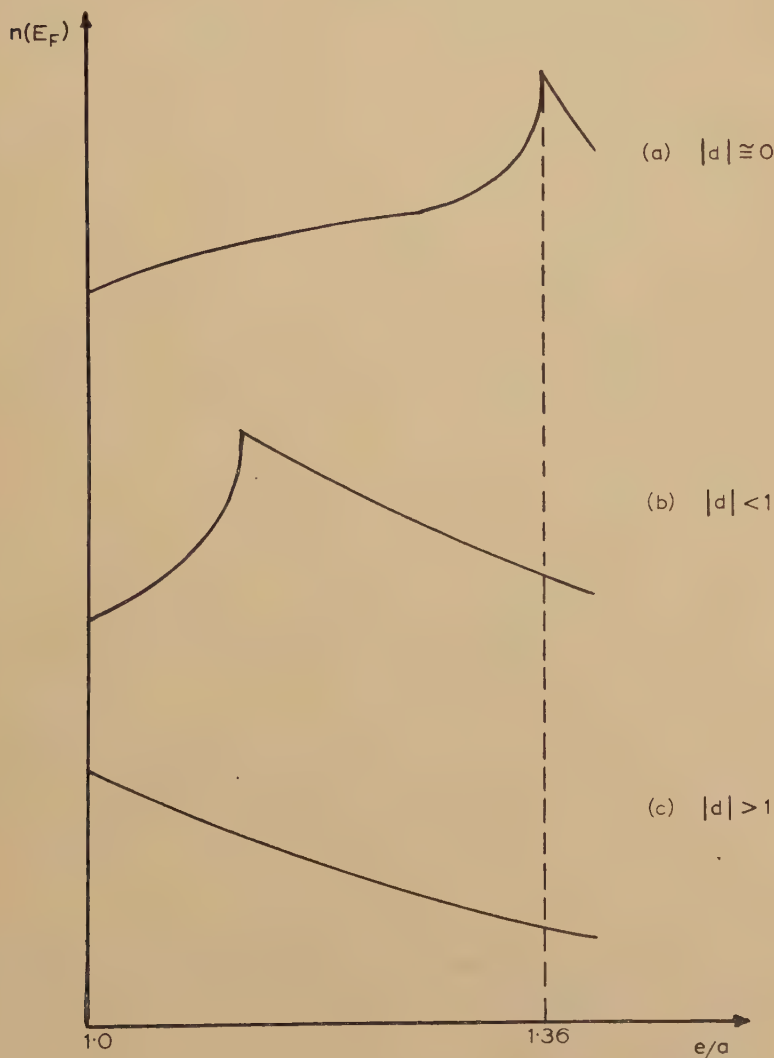


Density of states  $n(E)$  as a function of energy  $E$  (schematic).  $E_c$  is the energy of contact and  $E_F$  the Fermi level of the pure metal (half-filled band). The distortion of the band structure is small in (a) with  $|d| \ll 1$ , and large in (b) with  $|d| > 1$ .

The peak is more pronounced when the distortion of the band structure is small (fig. 3 (a)) than when it is large (fig. 3 (b)). In the rigid band model of an alloy, the shape of the  $n(E)$  curve is independent of concentration. The dependence of  $n(E_F)$  on  $e/a$  in the alloy can thus be derived from the  $n(E)$  of the pure solvent, as in fig. 4. When  $|d|$  is small for the solvent and all the energy surfaces are nearly spherical, contact and the associated maximum in  $n(E_F)$  occur at  $e/a \simeq 1.36$  (fig. 4 (a)). As the  $|d|$  of the solvent increases, the maximum moves towards lower  $e/a$  (fig. 4 (b)) and vanishes entirely

when there is contact in the pure solvent,  $|d| > 1$  (fig. 4(c)). Comparing Rayne's experimentally determined  $n(E_F)$  for CuZn (1957 a) and CuGe (1958), fig. 1, with the predictions of the rigid band model, we would be led to suppose that (fig. 4(b)) contact occurs for  $e/a \gtrsim 1.1$  and does not occur for pure Cu. This is in direct contradiction to the experimental evidence presented in § 4 and demonstrates the inadequacy of the rigid band model, as mentioned already in § 1.

Fig. 4



Dependence of density of states at the Fermi level  $n(E_F)$  on electron to atom ratio ( $e/a$ ) in alloys according to the rigid band model. The vertical scales are arbitrary and are displaced for the three cases (a)  $|d| \approx 0$ , (b)  $|d| < 1$ , and (c)  $|d| > 1$  in the pure solvent.

There are two effects upon alloying in our scheme for the band structure. Firstly there is the filling up of the band and secondly the change in  $E_s - E_p$  from the effect of the  $\Delta_{sp}$  of the solute. The relevant  $\Delta_{sp}$  are shown in table 1. We restrict ourselves to the  $\alpha$ -phases and ignore for the present discussion the alloys of copper, silver and gold among themselves. We note from table 1, then, that whatever we alloy into copper, silver and gold has a larger  $\Delta_{sp}$  than the solvent metal. The effect of the alloying is therefore to raise the level  $E_p$  and lower  $E_s$  relative to one another. In copper where  $E_p < E_s$ , the effect is to reduce  $E_s - E_p$  and thus to make the band structure more nearly spherically symmetrical. In gold, however, we have  $E_s < E_p$ , and the effect of alloying is to increase the distortion of the Fermi surface. We shall defer discussion of silver for the present. Our interpretation of the observed density of states curve of CuZn and CuGe from *electronic specific heat* (fig. 1), is thus as follows. The steep initial rise corresponds to an initial reduction of the area of contact due to the band structure becoming more spherical, while the zone fills up elsewhere. It is not clear whether the Fermi surface pulls completely away from the zone boundary or remains just touching. In Rayne's data (fig. 1), there is a suggestion of a second peak at  $e/a \sim 1.3$ , which could be the Fermi surface returning to the zone faces after pulling away at  $e/a \sim 1.1$ . In either event, the energy surfaces continue to become more nearly spherical as the concentration increases. Accordingly, when contact exists at the higher values of  $e/a$ , there is an increasingly rapid fall of  $n(E)$  with  $E$  and hence of  $n(E_F)$  with  $e/a$  (fig. 4).

Although the Knight shift is proportional to  $n(E_F)$  and hence to the electronic specific heat, we do not expect a corresponding effect in the *Knight shift*. The reason is that the  $\psi_k$  on the zone faces which are responsible for the break in the electronic heat curve are purely p-like states and give no contribution to the Knight shift. The latter is therefore expected to vary smoothly and rather less than  $n(E_F)$  with concentration, in agreement with the observations on CuAl† and on CuZn (Bloembergen and Rowland 1953). However, as discussed by these authors, quadrupole effects complicate the interpretation of the resonances in these alloys. The *ideal electrical resistivity* of CuZn also shows an anomaly near a 5% concentration of Zn like that in the specific heat (fig. 1) (Lomer and Rosenberg, private communication); this is to be expected if the relaxation time varies inversely as  $n(E_F)$  (compare eqn. (21)).

Guthrie (1958) has made heat capacity measurements on the alloys  $\text{Cu}_{(1-2x)}\text{Ni}_x\text{Zn}_x$  below 4.2°K for  $x \simeq 0.03$  and 0.08. He finds that  $\gamma$  increases rapidly with  $x$  and is approximately 20% higher than for pure Cu at  $x \simeq 0.03$ . These alloys have the same  $e/a$  as pure Cu so that a change in  $\gamma$  can be caused only by distortion of the band structure. Guthrie's results thus afford further evidence of the breakdown of the rigid band model. Conduction

† The data quoted by Knight (1956, table VII) show a small anomaly near 5% aluminium concentration. This anomaly is introduced through various corrections to the raw data (Teeters 1955) which exhibit no such effect.



electrons presumably avoid cells containing Ni atoms, which have a neutral  $d^{10}$  configuration. The distortion of the band structure by the change in  $\Delta_{sp}$  should therefore be similar to that in  $\text{Cu}_{(1-x)}\text{Zn}_x$  for small  $x$ , whereas in the latter  $\gamma$  is only 7% higher than for pure Cu at  $x \simeq 0.03$ . The filling up of the band in the CuZn alloys tends to increase the area of contact and reduce  $\gamma$ . It is the absence of this effect which leads to the more rapid rise of  $\gamma$  in the ternary alloys<sup>(10, 11)</sup>.

Values of  $n_\alpha$ , the value of  $e/a$  at the boundary of the  $\alpha$ -phase, are listed in table 7 for alloys of the noble metals having favourable size factors. The evident constancy of  $n_\alpha$  for the Cu and Ag alloys was discovered by Hume-Rothery and co-workers in 1934 (Hume-Rothery *et al.* 1934). An interpretation of this remarkable rule was put forward by Mott and Jones

Table 7. Electron to Atom Ratio  $n_\alpha$  at the Limit of Solubility in the  $\alpha$ -Phase

alloy	$n_\alpha$	$\eta$ (eV)	alloy	$n_\alpha$	$\eta$ (eV)	alloy	$n_\alpha$	$\eta$ (eV)
CuAl	1.40	4.6	AuCd	1.33	1.0	AgCd	1.43	3.0
CuGa	1.39	6.1	AuAl	1.31	3.1	AgZn	1.40	4.0
CuZn	1.38	4.0	AuZn	1.30	2.0	AgAl	1.40	4.8
CuGe	1.34	3.7	AuIn	1.26	4.2	AgIn	1.40	5.7
CuAs	1.27	3.6	AuGa	1.25	4.8	AgGa	1.36	6.3
			AuHg	1.20	4.0			
			AuSn	1.21	1.2	AgAs	1.35	3.7
			AuGe	1.09	2.4	AgSn	1.34	2.4
			AuSb	1.05	1.6	AgGe	1.29	3.7
						AgSb	1.29	2.9

Only alloys with favourable size factors are listed. Values of  $n_\alpha$  are taken from Raynor (1949). Values of  $\eta$  are calculated from eqn. (24) and the values of  $\Delta_{sp}$  in table 1.

(1936, Konobejewski 1936) which runs, in essence, as follows. The various contributions to the free energy of an alloy tend to vary relatively slowly with  $e/a$  except for the energy  $E_B$  associated with the filling of the band. The variation of the latter with  $e/a$  is given by

$$\frac{dE_B}{d(e/a)} = E_F, \quad C = \frac{d^2E_B}{d(e/a)^2} = \frac{dE_F}{d(e/a)} = \frac{1}{n(E_F)} \dots \dots (23)$$

If  $n(E_F)$  suddenly decreases as  $e/a$  increases, the curvature  $C$  of the free energy has a sharp minimum versus  $e/a$ . Phase transformations then occur at values of  $e/a$  very near that corresponding to the minimum in  $C$  unless the second phase has an unusually low or high free energy. There is a sharp drop in  $n(E_F)$  and hence a sharp minimum in the curvature at an  $e/a$  of 1.36 if the energy surfaces are nearly spherical and the band is rigid (fig. 4(a)). Thus values of  $n_\alpha$  should cluster about 1.36, in agreement with

experiment (table 7). We must modify this interpretation of the Hume-Rothery rule so that it no longer rests upon the rigid band model and becomes consistent with what we now know about the band structures of the pure metals.

The essential point of the above argument is that the curvature (23) rises sharply if the density of states drops sharply as  $e/a$  increases. It does not matter what the band structure is like before this decrease in  $n(E_F)$  sets in. Thus in Cu, where the large  $\Delta_{sp}$  of the solute atoms raises the energy  $E_p$  ( $E_p < E_s$  for Cu) and makes the band structure more nearly spherical on alloying, the original explanation of the Hume-Rothery rule is probably correct despite the contact in pure Cu. In support of this contention Rayne's results (fig. 1) indicate that the area of contact at least does not become large in CuZn and CuGe before the phase boundary is reached and there is a suggestion of a drop in  $n(E_F)$  before the phase boundary of CuZn. Quite clearly, the smaller the value of  $\Delta_{sp}$  of the solute and consequently the less spherical the energy surfaces, the smaller must be the value of  $n_x$ . The parameter pertinent to such effects is shown in Appendix C to be

$$\eta = \left(1 + \frac{1}{z-1}\right) [(\Delta_{sp})_{\text{solute}} - (\Delta_{sp})_{\text{solvent}}]. \quad . \quad . \quad . \quad . \quad (24)$$

The valency  $z$  of the solute enters eqn. (24) to scale the effect to the electron per atom ratio. As shown in table 7, the correlation is excellent in the series Cu(Zn, Ga, Ge, As): the larger  $\eta$ , the larger  $n_x$ . Only CuAl is out of order, presumably because Al comes from quite a different region of the periodic table and has no d-shell. Since the effect of the d-shell is to raise  $E_s$  relative to  $E_p$ , its absence is equivalent to an enhancement of the  $\Delta_{sp}$  of Al. In gold alloys, on the other hand, the fact that  $E_s < E_p$  for the pure metal means that the Fermi surface is distorted even more on alloying because of the larger  $\Delta_{sp}$  of the solute. The Fermi surface should touch the zone faces at relatively low values of  $e/a$  in agreement with the observation that  $n_x$  is considerably lower than 1.36 for gold alloys (table 7)†. The larger the value of  $\eta$  the lower the  $e/a$  at which contact occurs. Thus the correlation between  $n_x$  and  $\eta$  for gold alloys should be just the reverse of that found for copper alloys. Table 7 shows this to be the case for alloys of gold containing di- and trivalent solutes (those listed above the blank line). The gold-aluminium alloy is only slightly out of order and in the direction opposite to that predicted by the d-shell argument. A high free energy of the second phase for both CuAl and AuAl alloys would account for this behaviour. A low free energy of the second phase (electrochemical effect, Raynor 1949) is presumably responsible for the low values of  $n_x$  of the gold alloys containing tetra- and pentavalent solutes (those listed below the space in table 7) and, to a much lesser extent, for that of AuHg. In general, the values of  $\eta$  are small for tetra- and pentavalent solutes with gold and silver as solvent so that the band structure deforms only slightly through

† We can see no basis in the present theory of metals for Raynor's (1949) alternative explanation in terms of promotion of d-electrons to the conduction band.

changes in  $\Delta_{sp}$ . Other influences upon  $n_x$  can thus become relatively more important for these alloys.

We have used  $\eta$ , eqn. (24), as a measure of the effect of the change in  $\Delta_{sp}$  from alloying. However, the argument of Appendix C gives only a first approximation to the dependence of  $\Delta_{sp}$  on  $e/a$ . The correlation between  $n_x$  and  $\eta$  for solutes of the *same* valence is unaffected by this uncertainty. The sequences AuCd–AuZn–AuHg, AuAl–AuIn–AuGa, and AuSn–AuGe all do show the decrease in  $n_x$  with increasing  $\eta$  expected for gold alloys.

The above discussion demonstrates the significance of the band structure of the solvent metal and of the high  $\Delta_{sp}$  of the solute in determining the values of  $n_x^{(12)}$ . There are of course divers other well recognized factors influencing  $n_x$  (Raynor 1949) which are of far greater significance for some alloys. Of these, we have already alluded to the effect of the value of the free energy of the second phase. The large strain energy introduced when the atomic radii differ by 15% or more is another factor and is presumably responsible for the low values of  $n_x$  for CuCd, for example (Raynor 1949). The curious fact that  $n_x$  is very much lower for CuCd than for CuIn, CuSn and CuSb despite the small change in size factor has been attributed to the smaller ionic radii of the atoms of higher valence (Raynor 1949, p. 9). However, the increase of  $n_x$  from 1.02 for CuCd to 1.22 for CuIn may very well have something to do with the increase of  $\eta$  from 1.5 to 1.9 eV, i.e. the band structure is more nearly spherical for the CuIn alloys.

There is another influence upon the change in  $n_x$  between the valency two and valency three solutes. In the alloy the additional nuclear charge of a solute atom is screened by a cloud of electrons that is attracted round the atom. For slowly varying potentials, the screening is determined purely by the states at the Fermi level (Fiedel 1954), and we take this to apply approximately to the noble metal alloys although the condition of 'slowly varying' is not really fulfilled. We also suppose that the charge cloud round a solute atom will tend to simulate the configuration of the free atom because the exclusion principle and other forces enter in a similar way. Now in gold the states at the Fermi level have predominantly s-like character so that in AuCd the cadmium atoms have no difficulty building up their  $(5s)^2$  charge cloud, resulting in a relatively high  $n_x = 1.33$ . However in AuIn the indium atoms have difficulty in building up a  $(5s)^25p$  configuration due to the paucity of p-character in the  $\psi_k$  at the Fermi level, resulting in a high energy and low  $n_x = 1.26$ . A similar drop occurs between AuZn ( $n_x = 1.30$ ) and AuGa ( $n_x = 1.25$ ). This contrasts with the situation in copper where the  $\psi_k$  at the Fermi level have predominantly p-character, and where consequently there is no drop in  $n_x$  between CuZn ( $n_x = 1.38$ ) and CuGa ( $n_x = 1.39$ ) and between CuCd and CuIn. A related argument leads to the same conclusions when bound states (Friedel 1954) occur.

Another effect which may play a role in determining  $n_x$  is the change in lattice constant  $a$  upon alloying. According to eqn. (13), an increase in lattice constant  $a$  decreases  $E_s$  relative to  $E_p$ . Thus for Cu a decrease in  $a$  tends to distort the band structure and reduce  $n_x$ , whereas for Au the reverse



is true. However, rough estimates of this effect based on the reasoning leading to eqn. (13) suggest that it is less important than the change in  $\Delta_{sp}$  <sup>(13)</sup>.

For silver we proposed above a nearly spherical Fermi surface, but were unable to confirm the proposal by appeal to experiments on the pure metal. If the Fermi surface is nearly spherical, the rigid band model should work fairly well and the original explanation of the Hume-Rothery rule apply. The relatively large number of silver alloys for which  $n_x$  is high (table 7) supports this conclusion. It is also in accordance with the fact that the Knight shift in AgCd, AgIn, AgSn, AgSb depends to a good approximation on the electron per atom ratio only (Rowland, private communication). The temperature dependence  $\chi_{77^\circ} - \chi_{4.2^\circ}$  of the total susceptibility of AgZn shows a very marked narrow peak at 30% concentration (Meyer and Weiner 1957), which we suggest is associated with the Fermi surface contacting the zone faces. The fact that the concentration of 30% is near that for a spherical Fermi surface (36%) is quite in accordance with our model. We also proposed above that in silver  $E_p < E_s$ , which is consistent with the absence of a peak in the Knight shift at  $e/a = 1.30$ . The decrease in the Knight shift with increasing concentration is consistent with the approach of the Fermi surface to states of purely p-character near  $E_p$ . However, Drain (1957) has given an alternative interpretation which suggests that the requirement of local electrical neutrality may be the dominant factor in the decrease of the Knight shift in AgCd with concentration. The correlation of  $n_x$  with  $\eta$  in table 7 resembles that for gold rather than copper, and there is a decrease of  $n_x$  in passing from a di- to a trivalent solute. Further, the values of  $\xi_{Ag}$  in (22) lie closer to those of  $\xi_{Au}$  than those of  $\xi_{Cu}$ . These suggest that  $E_s$  is lower than  $E_p$ , and we have been unable to reconcile this with the absence of any peak or other zone boundary effect in the Knight shift measurements. The considerations of §2 definitely indicate that the  $E_s - E_p$  of Ag should be intermediate between that of Cu and that of Au. Thus if  $E_s - E_p < 0$  in Ag, it cannot be very large and the distortion should be less than that in Au. Thus the situation remains confused for silver except that the alloy evidence, as far as it goes, favours a nearly spherical Fermi surface.

Measurements of the temperature dependence of the total susceptibility have also been made on CuZn and AuZn alloys (Meyer, private communication). The CuZn shows a peak of 10–20% concentration, associated with the Fermi surface tending to pull away from the zone faces just as is the change of slope in the electronic specific heat (fig. 1). Very preliminary experiments on AuZn show a large and very sharp peak at a concentration less than 10%. If the Fermi surface in gold is very distorted but not quite touching the zone faces, this peak again receives a natural explanation in terms of contact<sup>(14)</sup>.

## § 6. DOUBTS, CERTAINTIES AND SUMMARY

The results of the comparison of our scheme with the experimental evidence for the alkali metals are quite satisfactory. It seems firmly

established that the Fermi surface is very nearly spherical in sodium and somewhat more distorted in potassium, with the distortion increasing considerably as one goes to rubidium and then to caesium. In lithium the shape of the soft x-ray emission spectrum seems to demand that the distortion is so great that the Fermi surface actually touches the zone boundary, and this accounts very naturally for the other anomalous electronic properties of lithium.

In § 4 and § 5 we have proposed a model of the band structure of the noble metals and their  $\alpha$ -phase alloys, and we have shown how this model allows a natural qualitative interpretation of a considerable range of experimental data. Our purpose in this section is to explore the possibility of alternative models and to ask "To what extent do the data demand one particular model rather than another?"

As regards copper, the anomalous skin effect measurements do demand a very distorted Fermi surface, which may touch or may just not touch the zone faces but very probably does (Pippard 1957). The optical and thermal data then decide quite definitely in favour of considerable contact (Cohen 1958). However the anomalies at 10% concentration in the alloys can be explained on either model. There are two effects on alloying, namely the change in  $E_F$  and the filling up of the band structure, the former tending to make the Fermi surface pull away from the zone faces and the latter having the opposite effect. We cannot predict definitely which will predominate, so that as regards the alloy properties alone we can have either contact initially with the Fermi surface pulling away from the faces, or no contact initially with the Fermi surface approaching the faces with increasing concentration. Our knowledge of the band structure of the pure metal of course decides in favour of the former picture. The p-like nature of the states on the zone faces is supported by several independent though in themselves inconclusive pieces of evidence, and a comparison between electronic specific heat and Knight shift of a spin- $\frac{1}{2}$  solute in the same alloy might give clearer evidence.

In the case of gold there are very few data from which to draw conclusions. The optical and thermal data (Cohen 1958) point definitely to a rather anisotropic Fermi surface, as does the fact that Jones' interpretation of the Hume-Rothery rule for the alloys does not work very well for gold. However, we have no means of telling how anisotropic the surface is and whether there is any contact with zone faces. As regards the s-like or p-like character of states on the zone face, the evidence of the Knight shift and of the values of  $n_\alpha$  in alloys is very suggestive that they are s-like but not really decisive. However, we regard there being very little doubt about it, in view of the very well documented fact that s-states in the very heavy metals are noticeably depressed in energy relative to p-states (§ 1). This should make the Knight shift a useful tool in future for studying when zone boundary effects occur in gold alloys, because of the s-symmetry of the relevant states on the zone faces, unlike the case of copper and possibly silver.

The situation in silver is the least clear. On the one hand some properties, notably the magnetoresistance (Olsen and Rodriguez 1957) and thermoelectric power (Mott and Jones 1936, p. 312), suggest in a general way that the Fermi surface is distorted by an amount comparable to that in copper and gold. On the other hand, the considerations of  $\Delta_{sp}$  in §4 suggest a nearly spherical Fermi surface, and in view of the success of such arguments in copper and gold and especially in the alkalis, they must be given some weight. The properties of the alloys are consistent with this, but do not provide any test for the same reasons as in copper. The optical and thermal data (Cohen 1958) are consistent with either a spherical Fermi surface, or considerable contact with the zone faces. It does not seem that the alloy properties will yield much help in deciding the question, and that more work on the properties of pure silver will be required.

Finally we have considered only one type of distortion of the Fermi surface, namely a bulging outwards in the direction of the nearest zone faces. Whereas this is the simplest and most likely type of distortion, only in the case of copper is there any clear evidence that the actual anisotropy is really like this (Pippard 1957).

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#### APPENDIX A

##### *Concerning the Wigner-Seitz Potential*

Howarth has made several calculations of the band structure of copper using different potentials and techniques (Howarth 1953 and 1955). It is noticeable that these all yield values of  $E_s - E_p$  which are less than our estimate of 1.4 eV and considerably less than the value of about 3.5 eV suggested by the amount of distortion of the Fermi surface deduced from experiment. We suggest that this may be explained by the following systematic error which appears to be involved in all band structure calculations, based on the Wigner-Seitz type of potentials (Mott and Jones 1936, p. 137). In the Wigner-Seitz potential, the exchange and correlation hole round an electron is always centred on the nearest atomic nucleus. This is a bad approximation for an electron midway between the nuclei, where it results in an exchange and correlation potential which is numerically too small. Thus for states with  $\mathbf{k}$  on the zone faces, the p-like electrons which are mainly in the region between the nuclei are



given too high a potential energy compared with the s-like states, resulting in a value of  $E_s - E_p$  which is too low. A rough estimate indicates that the error in  $E_s - E_p$  is of the order of 1 eV.

## APPENDIX B

### *Ratio of Ideal Electrical and Thermal Resistivities at Low Temperature*

In this Appendix we first discuss why  $D$  (eqn. (14)) furnishes information about the shape of the Fermi surface. Klemens' (1954 a, 1956) interpretation of the large values of  $D'$  (eqn. (15)) for Rb, Cs, Cu, Ag and Au runs as follows. In every collision with a phonon, an electron gains or loses an energy  $kT$  so that the time between collisions is the relaxation time for thermal conduction. On the other hand, the momentum transfer per collision is very small at low temperatures so that the time it takes an electron to reach the opposite region of the Fermi surface by many successive collisions is the relaxation time for electrical conduction. This effect is included in the existing theories of  $\rho_i(T)$  and  $W_i(T)$ , valid for spherical Fermi surfaces, so that  $D$  should be unity when the FS is spherical. However, if the Fermi surface touches the nearest zone faces, an electron reaching a point of contact emerges at once on the opposite region of the FS. The relaxation time for electrical conduction is thus decreased relative to that for thermal conduction by a factor estimated by Klemens to be about 10 for body-centred cubic metals and 5 for face-centred cubic metals. This effect is not included in the derivation of the numerical coefficient entering eqn. (14) for  $D$ ; consequently,  $D$  is increased by the same factor.

This argument of Klemens neglects two points. First and more significant, Umklapp processes are still of importance for electrons at those portions of a *spherical* Fermi surface nearest the zone faces down to the lowest temperatures for which  $\rho_i$  is measurable (Ziman 1954). An electron reaching one of those regions of the surface is soon scattered to the opposite region by an Umklapp process†. Thus the relaxation time for electrical conduction is reduced relative to that for thermal conduction, and by the above argument  $D$  can exceed unity even for a spherical Fermi surface. As the surface bulges towards the zone faces, the effect of Umklapp processes is enhanced and  $D$  increases. When the surface actually touches, Klemens' original argument applies and  $D$  increases still further. The second point is that even neglecting Umklapp processes, it is not necessary for the electron to reach the opposite region of the Fermi surface to terminate a free path. A mean free path is effectively terminated whenever the electron reaches a region of the FS where the velocity is appreciably reduced, e.g. by the Fermi surface bulging towards the zone faces. A value of  $|d| \sim 0.5$  would be sufficient for this to be of importance for  $D$ .

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† We are indebted to Dr. Ziman for pointing out to us the importance of Umklapp processes in this connection.

We now discuss our rough estimates of the ratio  $D'/D$ . At low temperatures, electrons are scattered by the lattice dilatation produced by long-wavelength phonons (see, e.g. Jones 1956). The transition probability for scattering by a given mode is therefore proportional to  $(\mathbf{q} \cdot \mathbf{u})^2$  where  $\mathbf{q}$  is the propagation and  $\mathbf{u}$  the polarization vector of the normal mode, and need not vanish for transverse modes in an elastically anisotropic crystal. A reasonable approximation to the average velocity of sound  $c_\rho$  entering the characteristic temperature  $\Theta_\rho$  of the electrical resistivity is

$$\left(\frac{1}{c_\rho}\right)^6 = \int \frac{d\Omega}{4\pi} \sum_j \frac{(\mathbf{q}_j \cdot \mathbf{u}_j)^2}{c_j^6} \dots \dots \dots (25)$$

as suggested by Blackman (1951)<sup>†</sup>. The corresponding approximation to the average velocity  $c_W$  is

$$\left(\frac{1}{c_W}\right)^4 = \int \frac{\Omega}{4\pi} \sum_j \frac{(\mathbf{q}_j \cdot \mathbf{u}_j)^2}{c_j^4} \dots \dots \dots (26)$$

In (25) and (26), the integration is over all directions of  $\mathbf{q}$  and the summation over the three modes for each  $\mathbf{q}$ . We have obtained what amount to little more than educated guesses for  $D'/D$  from crude, separate averages of  $(\mathbf{q} \cdot \mathbf{u}_j)^2$  and  $c_j^{-n}$ . The average of  $(\mathbf{q} \cdot \mathbf{u}_j)^2$  was computed by treating the elastic anisotropy as a perturbation, and the average of  $c_j^{-n}$  was taken to be the weighted mean of its values along the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$  and  $\langle 111 \rangle$  directions. The requisite elastic constants are known for Na, K, Cu, Au and Ag (de Launay 1956, p. 268), and the resulting values of  $D'/D$  are tabulated for these metals in table 8.

Table 8. Values of  $D'/D$

Metal	Na	K	Cu	Ag	Au
$D'/D$	1.1	1.6	1.1	1.2	1.4

## APPENDIX C

### $\Delta_{sp}$ in Alloys

It is difficult to state precisely what average of the  $\Delta_{sp}$  of solute and solvent,  $\bar{\Delta}_{sp}$ , should be used in calculating  $E_s - E_p$  in an alloy. We can, however, obtain a first approximation to  $\bar{\Delta}_{sp}$  by weighting the  $\Delta_{sp}$  of an atom according to the probability of finding an electron in a cell containing that atom. The probability of finding a given electron in a given cell is, on the average,

$$\frac{1}{1 + (z-1)c} \dots \dots \dots (27)$$

<sup>†</sup> Blackman actually averaged  $c^{-5}$ , which is incorrect,





observations on Li. Thus the change in the Knight shift with pressure cannot be taken as *conclusive* evidence for the Fermi surface of Li touching the zone faces.

(3) The discussion in the text concerns only the high temperature thermoelectric power. However, Ziman (1959) has calculated the contribution of phonon drag to the *thermoelectric power at low temperatures* and finds a large effect, the sign of which depends on a balance between Normal and Umklapp processes. The magnitude of the Umklapp contribution is very sensitive to the distortion of the Fermi surface. Upon analysing the observations of MacDonald *et al.* (1958) on the thermoelectric powers of the alkali metals below 80°K, Ziman finds that these are entirely consistent with our proposals for the Fermi surfaces.

(4) The relation between effective mass  $m^*$  and distortion parameter  $d$  given in eqn. (10) rests only on eqns. (1), (2) and (7), and not on the more questionable assumption (6). We therefore expect values of  $d$  calculated from

$$d = 5(m^* - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10')$$

using the QDM values of  $m^*$  (table 3, line 3) to agree even better with the experimental results than those given in table 3, line 1. Inspection of table 9 shows this to be the case.

Table 9. Values of  $d$  for the Alkali Metals)

Metal	Li	Na	K	Rb	Cs
$d$ from (10')	1.90	-0.10	-0.30	-0.45	-0.85

In particular we note that  $|d|$  is smallest for Na and that there is considerable contact in Li.

(5) Strictly speaking, this estimated value of  $\gtrsim 1.2$  for  $m^*$  should be compared not with  $m_0$  but with the effective mass on the spherical portion of the Fermi surface. The latter has been measured by Kip and Langenberg (private communication) in the cyclotron resonance experiment and found to be 1.3–1.4, in agreement with our estimate.

(6) Mott's (1953) interpretation of the  $L_3$  absorption spectrum (Cauchois 1953) mentioned above gives 3.5 eV for  $E_s - E_p$  for Cu. From this and contact, we infer that  $E_s - E_p \lesssim 3.5$  eV. Inserting  $d \gtrsim 1$  into (9) yields  $E_s - E_p \gtrsim 3.0$  eV, which agrees with the x-ray result.

(7) Ziman (1958) has argued that a polycrystalline sample of a metal having a cylindrical Fermi surface should have a linear dependence of transverse magnetoresistance on field as observed in the noble metals at high magnetic fields by Chambers (1956). This would suggest that the absence of saturation indicates contact in all three noble metals.

(8) Just as for the alkali metals (note 4), one can calculate values of  $d$  for the noble metals from (10') and the QDM values of  $m^*$  (table 5, line 4).

The values of  $d$  so obtained (table 10) for Cu and Au certainly are much smaller than those indicated by experiment. We suspect that the fault may lie more with the QDM calculations of Kambe (1955) than with eqn. (10') at least for Cu. For that metal, the value of  $E_s - E_p$  calculated from (9) by setting  $d = 1$  agrees with the x-ray absorption result, and the value of  $m^*$  similarly obtained from (10) agrees with the cyclotron resonance result. Still, there is reason to expect that eqns. (1), (2) and (7) are better for the alkali metals than for the noble metals, because they depend on having the size of the ion core small compared with the atomic volume. This condition is not nearly so well satisfied for the noble metals as for the alkali metals. In the noble metals, the ion cores are large and the  $d$ -band and conduction band overlap, so that the conduction band wave functions must contain a considerable amount of  $d$ -admixture through hybridization. The details of how this affects the band structure are not clear at present.

Table 10. Values of  $d$  for the Noble Metals

Metal	Cu	Ag	Au
$d$	0.07	-0.04	-0.05

(9) We discuss here the interrelation of the conduction and  $d$ -bands in the noble metals. The most familiar source of information is the *optical absorption* in the visible and ultra-violet, which has been interpreted in terms of excitation of  $d$ -electrons to the conduction band and of conduction electrons to the next empty band by Mott and Jones (1936, p. 147). In addition to these interband transitions which give an absorption increasing with energy near the interband absorption edge, there are other contributions to the absorption which fall with energy. The photon energy  $E_m$  at which the imaginary part of the dielectric constant  $D'' = 2nk$  has its minimum is thus an upper bound on the interband absorption edge; values of  $E_m$  derived from the optical constants reported by Schulz (1957) are given in line 1 of table 11. The absorption edge for conduction electron excitation would be the band gap  $|E_s - E_p|$  if  $|d|$  were unity or somewhat greater. The lower limits on the absorption edge in line 2 of table 11 are derived from (9) on this basis with  $d > 1$  for Cu, 1 or  $-1$  for Ag, and  $-1$  for Au. As  $|d|$  decreases from unity, the absorption edge increases monotonically and reaches the upper limits  $\frac{5}{4}k_F^2$  in line 2 of table 11 when  $|d| = 0$  ( $E_k = E_0 + k^2$ ). Comparison of lines 1 and 2 of table 11 shows that we can still follow Mott and Jones in attributing the interband absorption edge at 2.1 eV in Cu and Au to  $d$ -electron excitation even though we now know that contact or near contact of Fermi surface with zone boundary occurs in both metals. Assignment of the absorption edge at 3.1 eV in Ag to  $d$ -electron excitation is weakly favoured by our estimate of 0.04 for  $d$  (table 5) and by the likelihood of  $E_s$  lying below  $E_p$  if  $|d|$  were  $\sim 1$ ; Mott

and Jones, however, have assigned it to conduction electron excitation. The values of  $E_m$  are significantly less than our estimates of  $\sim 6$  eV for  $k_F^2/m^*$ , line 3 of table 11; the  $d$ -bands must therefore intersect the conduction band. The entries in line 1 are derived from the optical constants tabulated by Schulz (1957) and represent an experimental upper bound on the lowest interband absorption edge. In line 2, the lower limits equal  $|E - E_p|$  calculated from (9) with  $d > 1$  for Cu,  $= 1$  or  $-1$  for Ag and  $= 1$  for Au respectively. The upper limits equal  $\frac{5}{4}k_F^2$ , corresponding to  $d = 0$  and  $E(k) = E_0 + k^2$ . The values of  $m^*$  used in line 3 are taken from line 3 of table 5 for Ag and Au and calculated from (10) with  $d = 1$  for Cu. The entries in line 4 represent the separation from the absorption edge (Fermi level) of the main peak of the  $L$  absorption spectrum, attributed to the  $d$ -bands by Cauchois (1952, 1953). The estimate of the reduced width of this peak made by Cauchois (1953) for Cu is given in line 5. Line 6 gives the difference of the  $d^9s^2\ ^2D_{5/2}$  and  $\ ^2D_{3/2}$  term values of the free atoms (Moore 1952, 1958).

Table 11. Energy Parameters Relating to the  $d$ -bands of the Noble Metals (eV)

	Cu	Ag	Au
1. $E_m$	2.1	3.1	2.1
2. Limits for conduction band absorption edge	3.0, 8.9	2.3 or 3.4, 6.9	3.6, 7.0
3. Fermi energy, $k_F^2/m^*$	5.9	5.5	5.8
4. X-ray emission peak	3.0	$\sim 4$	—
5. Width of 4	1.2	—	—
6. Spin-orbit splitting	0.13	0.55	1.5

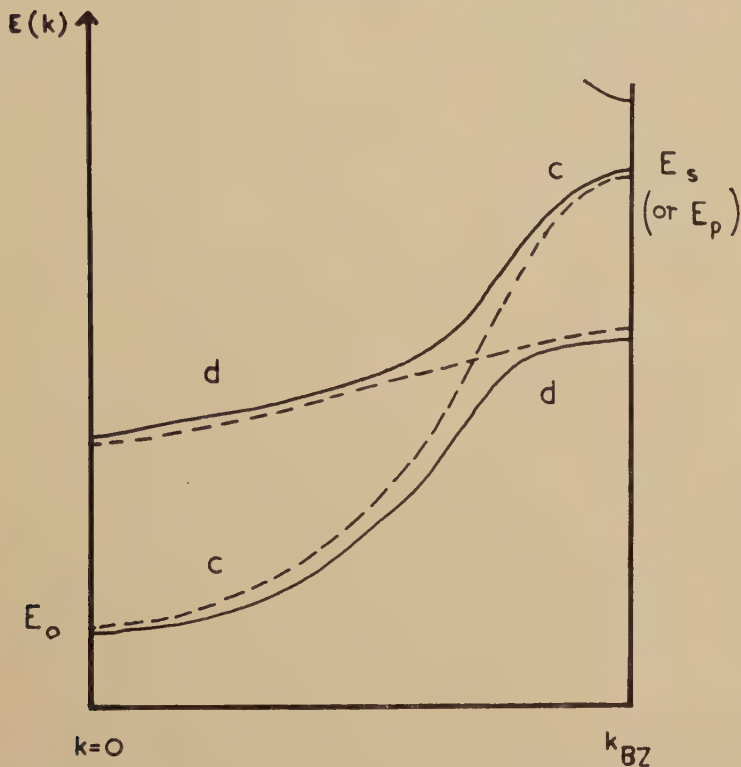
The *soft X-ray emission spectra* ( $L$ ) provide further evidence for the intersection of the conduction electron and  $d$ -bands. Cauchois has interpreted the  $L$  emission spectra of Cu (1953) and of Ag (1952) as arising in part from the  $d$ -bands. The main peak observed by Cauchois corresponds to some median energy in the  $d$ -bands, 3.0 eV below the Fermi level in Cu and 4 eV in Ag (table 11, line 4). The reduced width of this peak, 1.2 eV in Cu, gives a very rough estimate of the width of the  $d$ -bands. Comparison of lines 3 and 4 of table 11 shows that the conduction and  $d$ -bands intersect for Cu and Ag.

We may summarize the experimental evidence as follows. The  $d$ -bands appear to have a width of  $\sim 2$  eV in Cu and Ag and are centred about an energy  $\sim 3$  eV below the Fermi level in Cu and  $\sim 4$  eV in Ag. The top of the  $d$ -band comes  $\sim 2$  eV below the Fermi level in Au and in Cu, but we have no evidence concerning the width in Au. The fact that the ionic radius of Au practically equals half the interatomic separation suggests that the  $d$ -bands may be wider in Au than in Cu or Ag. The  $d$ -bands



intersect the conduction band in all three metals, as indicated schematically by the dotted curves in fig. 5 for one of the five  $d$ -bands. The dotted curves represent  $E(k)$  for the conduction band and a single  $d$ -band along an arbitrary direction in  $k$ -space. The bands intersect because interaction between the conduction electrons and  $d$ -electrons has not been treated properly. When the interaction is properly included hybridization results, and the crossover is removed, as represented by the solid curves.

Fig. 5



Hybridization between conduction band (c) and  $d$ -band (d).

The notion of intersecting conduction and  $d$ -bands is, of course, oversimplified. Such crossover degeneracies as displayed by the dotted curves in fig. 5 can only occur, if at all, along certain symmetry directions. In general, the crossover degeneracies are lifted by hybridization of the conduction and  $d$ -bands, as indicated by the solid curves in fig. 5. What with five  $d$ -bands and the importance of spin-orbit coupling (see line 6 of table 11), the actual structure of the conduction *cum*  $d$ -bands must be very complex. However, the top of the  $d$ -bands still lies several electron volts below the Fermi level and the key levels  $E_s$  and  $E_p$  of fig. 1. We can

therefore generalize our description of the conduction band to include hybridization with the  $d$ -band for energies near and above the Fermi level. States  $\psi_k$  away from the zone face can no longer be represented by single OPW's, but include atomic  $d$ -orbitals as well. However at the centre of the nearest zone face,  $\psi_p$  being odd is not hybridized with the  $d$ -orbitals, which are even. Thus the effect of hybridization in our scheme is primarily to increase  $E_s$  relative to  $E_p$ . This effect should be significantly larger for Cu and Au than for Ag according to line 1 of table 11.

(10) This interpretation of Guthrie's results is too naïve. It completely neglects the influence of the Ni atoms upon the conduction band through the hybridization discussed in the preceding note. Dr. Guthrie has pointed out to us that the change in  $\gamma$  caused by adding small amounts of Zn and Ni together to Cu is about equal to the sum of the changes caused by adding the same amount of Zn (Rayne 1957a) and Ni (Guthrie, Friedberg and Goldman, unpublished work reported by Pugh *et al.* 1957) separately. This is in accord with Friedel's ideas of the independent effects of impurities in dilute alloys (Friedel 1954). Thus, the concentration dependence of  $\gamma$  in  $\text{Cu}_{1-2x}\text{Ni}_x\text{Zn}_x$  neither contradicts nor lends support to our interpretation of that in  $\text{Cu}_{1-x}\text{Zn}_x$ . The argument that Guthrie's results demonstrate the breakdown of the rigid band model, of course, remains correct.

(11) Friedel (1954, 1956, de Faget de Casteljau and Friedel 1956) has developed an interesting model of dilute CuNi alloys which yields a simple interpretation of their  $\gamma$  values. As Friedel's model also sheds light on the role of the  $d$ -bands in the deformation of the band structure of alloys with the elements from the B-subgroups, we describe it briefly here. Let us first neglect hybridization of the conduction and  $d$ -bands. The  $d$ -level in atomic Ni is higher than that in Cu. Substituting a Ni atom for a Cu atom in the metal is therefore equivalent to introducing a local centre of repulsive potential as far as the  $d$ -electrons are concerned. This potential, if strong enough, splits off a localized  $d$ -state from the top of the conduction band. Bringing the conduction band back into the picture, we see that the localized state must be degenerate with states in the conduction band. Hence, it must be a resonant level rather than a bound state. Its effect is to increase the density of states in a region of energy given by the lifetime of the resonant level. If the resonant level lies near the Fermi level, it can cause a rapid increase in  $\gamma$  with Ni concentration such as is actually observed. The large residual resistivity and diamagnetism of the copper rich CuNi alloys can be explained similarly.

There are additional effects neglected by Friedel. Suppose the repulsion of the Ni atom for a  $d$ -electron were too weak to split off a bound state. The  $d$ -bands would then shift upwards in energy relative to the conduction band upon the addition of Ni, the conduction electron concentration simultaneously falling so that the crossover point in fig. 5 rapidly approaches the Fermi level. Since the effect of hybridization is to reduce  $dE/dk$  near the crossover, the density of states and therefore  $\gamma$  is higher than expected upon neglect of the  $d$ -bands. This effect is present even if the resonant

level is split off. In any case, the repulsion of a  $d$ -electron by a Ni atom decreases as the concentration of Ni in the alloy increases, and the resonant level gradually merges with the  $d$ -band. The resonant level may be regarded simply as enhancing the effect of hybridization.

Now let us apply Friedel's ideas to an alloy of a noble metal with a B-group element. In these elements the atomic  $d$ -level lies lower than in the noble metals. A local  $d$ -state may split off the bottom of the  $d$ -band. In either event, the effect of hybridization on the level  $E_s$  is diminished by an effective lowering of the energy of the  $d$ -bands. Since  $E_s$  is raised by hybridization,  $E_s$  tends to be lowered relative to  $E_p$  by alloying. The band structure of Cu becomes more nearly spherical, that of Au distorts further, and that of Ag is relatively little affected. Thus the effect of the  $d$ -bands is to give the same trends in the bandstructures of Cu and Au alloys as the  $\Delta_{sp}$  effect already considered.

(12) Dr. Friedel has pointed out to us that similar arguments could well be applied to the  $\beta$ -phase alloys of the noble metals, and would lead us to expect that the phase boundary (on the high concentration side) comes at a relatively low  $e/a$  when  $n_\alpha$  is low. There do not appear to be many alloy systems with favourable size factors, etc., where one can check this, and the order-disorder transition is a complication. Nevertheless, the few given by Raynor (1949) give no real evidence of this effect so we must conclude that other factors are dominant here.

(13) As a result of discussions with Professor Hume-Rothery and others about the alpha-phase boundary, we wish to add here the following appraisal of the theory in Mott and Jones (1936), that given by Jones (1937) and the present work. The explanation of the Hume-Rothery rule given by Mott and Jones (1936) is essentially the one outlined in §1, based on spherical energy surfaces and a rigid band model. The theory of Jones (1937) is a more detailed calculation of the free energy difference between the alpha and beta phases of copper alloys. He assumed a rigid band model and very distorted energy surfaces corresponding to a band gap of 4.1 eV obtained from the optical absorption edge. In this calculation, contact with the zone face comes at  $e/a = 1.04$ , but the alpha-phase boundary does not occur until  $e/a = 1.40$ . The low values of  $n_\alpha$  in the gold alloys is then explained as due to the electrochemical effect (Raynor 1949, Hume-Rothery *et al.* 1940). The silver alloys are not specifically discussed. Now the present work is not attempting to set up a complete theory of the alpha-phase boundary, and the importance of the electrochemical factor in general (particularly in the case of solutes with large  $z$ ) is taken for granted, as is the fact that when the energy surfaces are very distorted then the values of  $n_\alpha$  tend to be rather higher than  $e/a$  at contact. However, there are some pieces of circumstantial evidence which suggest that there is more to the phenomenon of the phase boundary than is considered by Jones (1937) and Hume-Rothery *et al.* (1940).

Firstly, a significant aspect of the Jones (1937) model is that the energies of the phases vary rather smoothly with concentration, and that



the phase boundary is determined by a detailed balance between the two phases. Thus we would expect the value of  $n_\alpha$  to be quite sensitive to all the gross simplifying assumptions in the model. In particular we can attach rather little weight to the actual number 1.40 given by the theory, and we would expect the value of  $n_\alpha$  to be quite sensitive to the difference between different solutes. Thus the Jones (1937) model does not adequately explain why the values of  $n_\alpha$  are in fact so remarkably nearly the same, (i) independent of the differences between different solutes, (ii) independent of the structure of the next phase, and (iii) the same for copper and silver alloys: nor does it explain (apart from suggesting that it is accidental) why the values of  $n_\alpha$  should cluster round the particular number  $\approx 1.36$  suggested by the free electron model. However, the original Mott and Jones' (1936) theory, coupled with the present work, can give an explanation of these facts because it suggests that there is one factor, namely the zone boundary effect, which to a first approximation dominates all other effects and precipitates the phase transition.

Secondly as regards the gold alloys, if their low values of  $n_\alpha$  are *predominantly* due to the electrochemical factor, then one would expect the values of  $n_\alpha$  to correlate with this factor. The electrochemical factor  $f$  is the difference between solvent and the solute in the electrochemical series, as measured say by their electrode potentials relative to hydrogen. In the following series we compare  $n_\alpha$  with  $f$  and also with our  $\Delta_{sp}$  parameter  $\eta$ , keeping  $z$  constant in the series in an attempt to eliminate other factors as far as possible.

	AuCd	AuZn	AuHg
$n_\alpha$	1.33	1.30	1.20
$f$	1.9	2.3	0.7
$\eta$	1.0	2.0	4.0

Thus the prediction that a large  $f$  produces a low  $n_\alpha$  is not borne out, the correlation being if anything in the opposite direction. However as already mentioned in the text, the values of  $n_\alpha$  correlate reasonably well with the parameter  $\eta$  as expected according to the  $\Delta_{sp}$  effect. In addition there is the matter of the change in  $n_\alpha$  between  $z=2$  and  $z=3$  solutes as mentioned in the text.

We conclude therefore that there is some circumstantial evidence which suggests that the  $\Delta_{sp}$  effect discussed in the text is also an important factor determining the position of the alpha phase boundary, in addition to the other factors reviewed by Raynor (1949). At present it is impossible to assess the relative importance of these factors, but the suggestion is that the original explanation of Mott and Jones (1936), coupled with the present work, could well be nearer the truth than the Jones (1937) model.

(14) Rayne has obtained a value of  $0.66 \pm 0.02$  millijoule per mole deg<sup>2</sup> for the  $\gamma$  of disordered Cu<sub>3</sub>Au, which is significantly less than the value of

0.738 derived by correcting the  $\gamma$  of pure Cu for the change in lattice parameter according to the free electron model (Rayne 1957b). In our scheme for the band-structure  $E_s - E_p$  and therefore  $d$  decreases as gold is added randomly to copper, with two consequences for  $\gamma$ . Firstly, the effective mass  $m^*$  decreases and with it the contribution to  $\gamma$  of the part of the Fermi surface away from the area of contact. Secondly, the Fermi surface does not contact the zone boundary at intermediate gold concentrations and  $\gamma$  is thereby further reduced. These two effects are presumably responsible for the low value of  $\gamma$  observed for disordered  $\text{Cu}_3\text{Au}$ . Carrying the argument further, we would actually expect the Fermi surface to be spherical at some concentration. Measurement of the dependence of electronic properties of disordered CuAu alloys on composition would be of particular interest in this connection. The CuAg, CuAu and AgAu systems all have  $e/a = 1$  and thus permit observation of effects due to distortion of the bandstructure only.

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## The Properties of the Saturated Helium Film

By L. C. JACKSON† and L. G. GRIMES

H. H. Wills Physical Laboratory, University of Bristol

### § 1. INTRODUCTION

IN this article an account will be given of the known properties of the relatively thick film which covers all solid surfaces in contact with liquid helium II or with the saturated vapour in equilibrium with the liquid. The information, as yet rather meagre, available on the properties of the film which exists above the  $\lambda$ -point will also be discussed. For an account of the behaviour of the film in equilibrium with helium vapour at pressures less than the saturated vapour pressure, the 'unsaturated film', the reader is referred to review articles by Long and Meyer (1953), by Daunt and Smith (1954) and by Atkins (1957 a).

### § 2. EARLY OBSERVATIONS

The earliest observation of a helium film phenomenon was made by Kamerlingh Onnes (1922). He had a small Dewar vessel containing liquid helium II, partially immersed in liquid helium II in an outer vessel and observed that the inner vessel always filled or emptied until the inner and outer liquid surfaces stood at the same height. Onnes commented that the speed of adjustment of the levels was striking and that the two levels then fell at the same rate. Onnes believed he was dealing with a distillation process but it is now known that the readjustment of the levels takes place by means of a mobile liquid film covering the walls of the inner Dewar vessel. The significance of the two levels remaining together as they fall does not seem to have been generally realized. Since the loss of liquid helium under the conditions of Onnes' experiment is almost wholly due to film transfer up the walls of the outer vessel, the observation is really an anticipation of the double beaker experiment of Daunt and Mendelssohn (1946 a) (see § 11).

The first suggestion of the existence of a helium film arose when Rollin (1936) found that the thermal insulation of a metal vessel, filled with liquid helium, decreased appreciably when the temperature was taken below the  $\lambda$ -point. His experiments led him to propose that on any solid surface in contact with liquid helium, there was present a thin film of liquid. This film was present at all temperatures corresponding to the liquid phase. The drastic change in the thermal insulation of the vessel

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† Present address : Royal Military College of Canada, Kingston, Ontario.

below the  $\lambda$ -point was considered to be due to an abrupt change in the thermal conductivity of the film at the  $\lambda$ -point. Experiments carried out in the years 1936–39 by Rollin and Simon (1939) indicated that the above interpretation of Rollin's earlier work was incorrect and proved without doubt that the high evaporation rate was entirely due to a thick *mobile* film present below the  $\lambda$ -point. The film flowed to the warmer parts of the apparatus, evaporated there and was continuously replenished from the bulk liquid. Blaisse *et al.* (1939) showed that the ratio of the loss of liquid by film flow to that by evaporation was about 4:1 and that by making a small constriction in the pumping tube the film flow could be reduced considerably without greatly increasing the pumping resistance. They were thus able to reach a temperature of  $0.8^\circ\text{K}$  with a pump of only 10 l/sec capacity.

A rough determination of the average thickness of the film was made by Kikoin and Lasarew (1938, 1939) by determining the volume of liquid required to cover a large area with film. They also showed that the temperature of any surface covered by the film was in close agreement with that of the bulk liquid.

Finally in a classical series of experiments Daunt and Mendelssohn (1938, 1939) placed the existence of the helium II film beyond doubt, showed its astonishing mobility and determined its principal properties.

### § 3. DETERMINATION OF THE THICKNESS OF THE HELIUM II FILM

The first determination of helium II film thickness by Kikoin and Lasarew (1938) consisted in measuring the volume of liquid helium required to cover a previously dry surface. The observed volume was only  $3 \times 10^{-3} \text{ cm}^3$ , giving an average film thickness of  $2.3 \times 10^{-6} \text{ cm}$ . The temperature, at which the observations were made, was not stated. These authors were the first to observe that the film was completely destroyed by illuminating the surface with a lamp near the cryostat.

Daunt and Mendelssohn (1939) allowed the film to form on a roll of copper foil by dipping a fine wire attached to the copper into liquid helium. They then removed the roll to a region at room temperature, where the film evaporated and measured the increase in volume of the liquid helium due to the condensation of the evaporated helium. A correction was made for the change in density of the displaced gas. The mean of their results gave an average thickness of  $3.5 \times 10^{-6} \text{ cm}$  with no systematic variation of thickness with temperature below the  $\lambda$ -point.

In deducing these thicknesses it has, of course, been assumed that the density of the liquid in the film is the same as that of the bulk liquid. With films about 100 atoms thick this is a reasonable assumption, but see page 452 for the discussion of Atkins and of Franchetti of the variation of the density over the cross section of the film.

In both these determinations the observed value is the thickness averaged over a considerable range of heights above the level of the bulk liquid. As the thickness of the film on a surface in contact with bulk

liquid must be expected to vary with the height, it is highly desirable to be able to determine this variation. In the later work by Atkins, by Picus and by Bowers, the variation of thickness with height could be derived from the observations. In the method used by Burge and Jackson the thickness at any height within the limits of the apparatus could be measured directly.

Atkins's (1950 a) determination of the film thickness was based on the following observation made originally by Allen and Misener (1939): when a beaker empties itself by film transfer the equilibrium position is approached with considerable momentum so that the inner level overshoots and then oscillates about its original position. Atkins showed that an expression can be derived for the period of these oscillations and from it the relation between film thickness and height. The difficulty in the development of the theory was the almost complete lack of precise information regarding the hydrodynamics of film flow. Thus certain assumptions had to be made such as that the velocity in the film at a fixed height was uniform over the film thickness and that the thickness and profile of the film were independent of the velocity†. The period of the oscillations was then shown to be

$$\tau = 2\pi \left[ \frac{\rho}{\rho_s} \frac{r}{2g} \left( 1 + \frac{r}{R} \right) \int_0^l \frac{dH}{d} \right]^{1/2}$$

where  $r$  and  $R$  are the inner and outer radii of the beaker and  $l$  is the height of the rim of the beaker above the bath level. The variation of  $d$ , the film thickness with  $H$ , the film height, could then be deduced from observations of the period as  $H$  varied from 1 cm to 5 cm. Beakers of two types of glass were used, number 1 soda glass, number 2 lead glass and the thickness at the same temperature and height was different in the two cases by about 30%. The results, which are included in table 1, could be represented by the expression  $d = k/H^n$ . For beaker number 1 the observed film thickness at 1 cm height varied from about  $1.5 \times 10^{-6}$  cm at  $1.1^\circ\text{K}$  to  $2.4 \times 10^{-6}$  cm at  $2.0^\circ\text{K}$ .

More recently Picus (1954) investigated film flow at very small differences of height and deduced film thicknesses from the observed oscillations in a manner similar to Atkins. His value for  $k$  was  $2.5 \times 10^{-6}$  and for  $n$  was 1 or 0.5 dependent on the way in which the oscillations were produced. He also concluded that the thickness of the moving film was different from that of the static film.

Bowers (1953 b) has made a determination of the film thickness by weighing the film with the aid of a microbalance. A corrugated aluminium foil of such a shape as to give a large surface area without risk of holding bulk liquid by capillarity was suspended by the microbalance by a fine wire. Another fine wire attached to the bottom of the foil dipped into

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† While later work has rendered the first assumption highly probable, it is now known that the film thickness varies somewhat with the velocity but a re-evaluation of Atkin's data to allow for this would be very difficult.



liquid helium II. By weighing the foil and film for various depths of immersion of the feeding wire, it was possible to find an expression giving

Table 1

Author	Temperature (°K)	Range of heights (cm)	$k$ $\times 10^{-6}$	$n$
Atkins	No. 1 1.47	0.5-5.0	1.67	0.14
	No. 2 1.47	0.5-1	2.2	$\sim 0.5$
	No. 2 1.47	1-4.5	2.2	$\sim 0.1$
Picus	Temp. indep.	very small	2.5	1.0 ; 0.5
Bowers	Temp. indep.	0-7.6	11.8	0.5
Burge and Jackson	1.1	0.15-1.5	1.9	0.28
	2.1	0.15-1.5	1.9	0.4
Ham and Jackson	1.32	0.4 -1.6	3.15	0.38
	2.05	0.4 -1.6	3.15	0.43

the variation of  $d$  with  $H$ , which when averaged over the height range covered by the 7.6 cm long foil, reproduced the observed mass of the film. Bowers's results could be represented by

$$d = 11.8 \times 10^{-6} / H^{0.5}$$

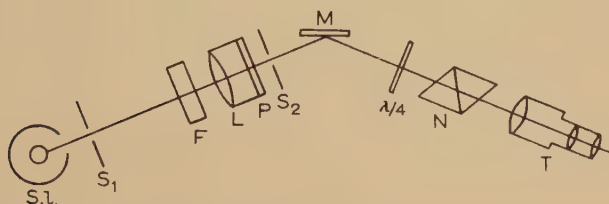
though Bowers was careful to point out that this did not necessarily imply that the thickness at 1 cm was  $11.8 \times 10^{-6}$  cm as the thicknesses were all averaged over heights which were much larger than 1 cm and the index in  $H^n$  may not be the same at large heights as at small. The observed thicknesses were almost independent of the temperature. When the tail wire was not in contact with the liquid the thickness of the film decreased to about  $2.2 \times 10^{-6}$  cm, almost independent of height and of temperature.

Knudsen and Dillinger (1954) and Dillinger (1955) have described a series of experiments in which a He II film was allowed to form on a long spiral of copper wire and from which information could be obtained of the rate at which the film advances over the wire and the amount of liquid required to form the film when the wire was (1) initially dry, (2) covered by a helium film of less than the full thickness. It was concluded that the film is more stable, less readily evaporated, at certain thicknesses than others and that the static film on a vertical surface may have a step-like structure. No explanation of the observations has been put forward yet nor is there any confirmation of the different stabilities from adsorption studies. Step-like films have been observed by Ham and Jackson (1957) but only when a strong Taconis resonance oscillation was present in the gas column above the substrate on which the film was observed. There is,

however, no apparent reason for suspecting a similar oscillation to have been present in Knudsen and Dillinger's experiments.

Rothen (1945) and Rothen and Hanson (1948, 1949) have described an optical method for the determination of the thickness of thin films of protein and this method has been adapted by Burge and Jackson (1951) to the helium film problem. The method was based on the fact that when plane polarized light is reflected from a polished metal surface the reflected light is elliptically polarized. If now the metal surface is covered with a thin layer of a transparent material the ellipticity of the light is different and the change in ellipticity is a measure of the thickness of the added film. Sodium light passed through a filter of heat absorbing glass F and was then polarized at  $45^\circ$  to the plane of incidence on the mirror M by the polaroid P. The reflected light passed through a mica compensating plate  $\frac{1}{4}\lambda$ , a Nicol prism N and a telescope T. As in Rothen's work the

Fig. 1



Optical arrangement. S.L. sodium lamp;  $S_1$ ,  $S_2$  slits; F, filter of heat absorbing glass; L, lens; P, polaroid; M, mirror;  $\lambda/4$ , mica compensating plate; N, nicol prism; T, telescope.

accuracy, with which the setting of the Nicol prism could be made, was greatly increased by the following half-shade method. The upper part of the stainless steel mirror was coated by the Langmuir trough technique with a monomolecular layer of barium stearate and the lower part with a similar layer three molecules thick. There was thus a sharply defined step in the thickness of the layer equal to  $48\text{ \AA}$ . In general the illumination of the two areas of the mirror as seen at the telescope was not the same, but settings of the  $\frac{1}{4}\lambda$  plate and the Nicol prism could be found at which the two areas appeared equally dark and the sharply defined boundary disappeared. The lower end of the mirror dipped into liquid helium and readings of the position of the Nicol prism were made when the temperature was just above the  $\lambda$ -point, say  $2.3^\circ\text{K}$ , and then at some desired temperature below the  $\lambda$ -point. This procedure was adopted as being simple to carry out and because, at the time, it was thought that the thickness of the helium film above the  $\lambda$ -point was very small. The shift of the Nicol prism was of the order of  $100$ – $200$  minutes of arc, measurable to within  $\pm 8$  min. With improvements incorporated later, Ham and Jackson

(1957), the settings could be made with a probable error of  $\pm 1$  min of arc. The thickness of the film was thus measured at the position of the 1-3 boundary and the height of the latter above the liquid helium surface slowly increased with time as the result of the fall of the liquid level by evaporation and film transfer up the walls of the cryostat. Various precautions were taken to prevent extraneous heat input into the mirror. The plane mirror was supported from below on a thin rod attached to the top of the cryostat so that heat conducted down the support was absorbed by the bath liquid and not by the mirror. The mirror was further surrounded by a cylindrical radiation shield of copper the lower end of which dipped into the liquid helium. Slits were cut in the shield for the incident and reflected beams. A small glass beaker filled with liquid helium was attached to the support and served to reduce the evaporation of the bath liquid to  $1\text{--}2\text{ cm}^3$  per hour. The observations were made in a completely darkened room. While it was thought that relative values of film thickness given in this investigation were reasonably correct, the absolute values were only provisional. The calibration of Nicol shift in terms of film thickness was made by assuming values for the refractive indices of liquid helium, barium stearate and stainless steel, and using the rather complicated formula for the case of a metal covered with two transparent layers.

It was found that the film thickness varied slightly with the temperature and could be represented by the formula  $d = k/H^n$  with  $k = 1.9 \times 10^{-6}\text{ cm}$  at  $1.5^\circ\text{K}$  and  $n$  varying from 0.28 at  $1.1^\circ\text{K}$  to 0.4 at  $2.0^\circ\text{K}$ . The work showed that the optical method was capable of good accuracy if further developed. Preliminary observations were also made on a number of other film properties and are recorded by Burge (1949).

The work has been repeated by Ham and Jackson (1957) with various improvements which made the optical arrangements more sensitive and ensured the constancy and uniformity of the temperature around the mirror. The mirror was mounted from below in a cylindrical glass chamber with copper ends into which purified helium gas could be condensed. The chamber was surrounded by a radiation shield and was completely immersed in liquid helium in the cryostat. Readings of film thickness could therefore be made at any desired constant height and temperature and could be repeated as many times as desired. The effect of varying purity of the helium could be studied and the degree of purification necessary to obtain repeatable results could be ascertained. A definitive calibration was made by determining, with the same apparatus, the complex refractive index of the 1- and 3-areas of the mirror at the temperature used in the observations and then using the simple formula for one layer of transparent material on a metal surface. The only quantity not directly measured was the refractive index of the helium film and for this the value obtained for bulk liquid was assumed.

In addition the effects of the double refraction due to residual strains in the Dewar vessels and that due to change of pressure in the condensation chamber were studied and corrections applied†. The observed film



thickness at a constant height again increased slightly with increase in temperature. A plot of  $\log d$  against  $\log H$  showed that at  $2.05^\circ\text{K}$  the thickness could be represented by the power law  $d = k/H^{1/z}$  ( $1/z = n$ ) with reasonable accuracy but that the fit with the formula became steadily worse at lower temperatures, see table 2. The thickness is shown as a function of the height for various temperatures in fig. 2.

Fig. 2

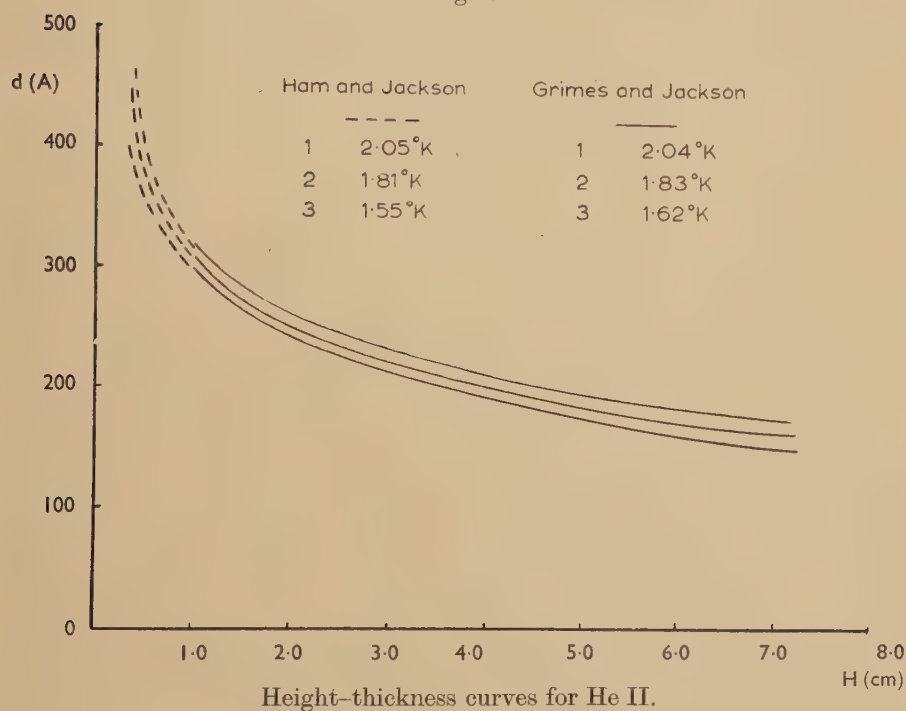


Table 2

$T$ (°K)	$10^6 k$ (cm)	$z$
2.05	3.15	$2.26 \pm 0.02$
1.81	3.10	$2.36 \pm 0.10$
1.55	3.02	$2.48 \pm 0.35$
1.32	2.96	$2.59 \pm 0.45$

† There are theoretically two different positions of the Nicol prism at which the illumination is the same on the 1- and 3-areas of the mirror: Burge and Jackson (1951) used the position which gave the larger Nicol shift but unfortunately the later work showed that this position shows the greater sensitivity to accidental double refractions, resulting in an appreciable change in the calibration.

These observations can be represented within the accuracy claimed for the data over the restricted range of height, 8 to 16 mm by the formula proposed by Atkins (1954).

$$H = \left(\frac{a}{d}\right)^3 + \left(\frac{b}{d}\right)^2$$

with the values of  $a$  and  $b$  given in table 3.

Table 3

$T$ (°K)	$10^6 a$	$10^6 b$
2.05	1.89	2.78
1.81	1.89	2.74
1.55	1.89	2.63
1.32	1.89	2.54

Jackson and Grimes (1957) have extended the observations to the height range 1–7 cm. For this purpose a new apparatus was constructed to accommodate the longer mirror and to make it possible to fill the cryostat with liquid helium from a storage vessel instead by means of a small Linde type liquefier incorporated in the cryostat. A calibration was determined for this new mirror including a different correction for the accidental double refraction since the liquid helium was surrounded by two Dewar vessels instead of three as in the work of Ham and Jackson. It is therefore gratifying that there is such a good agreement between the two sets of observations as shown in fig. 2. In the region where the height ranges overlap there is agreement to about 1%. The film thickness did not change when the helium condensed in the mirror chamber was obtained in the following three ways: (1) an evacuated reservoir was filled by drawing off the gas from the surface of liquid helium; (2) the gas so obtained was also passed through charcoal cooled with liquid nitrogen; (3) the gas was also passed through charcoal cooled with liquid hydrogen.

The results given in fig. 2 do not fit a simple inverse power law over the whole range. They are being compared with the expression deduced by Franchetti (1957)

$$H = \frac{a}{d^3} + \frac{b}{d^2} + \frac{c(T)}{d^2}$$

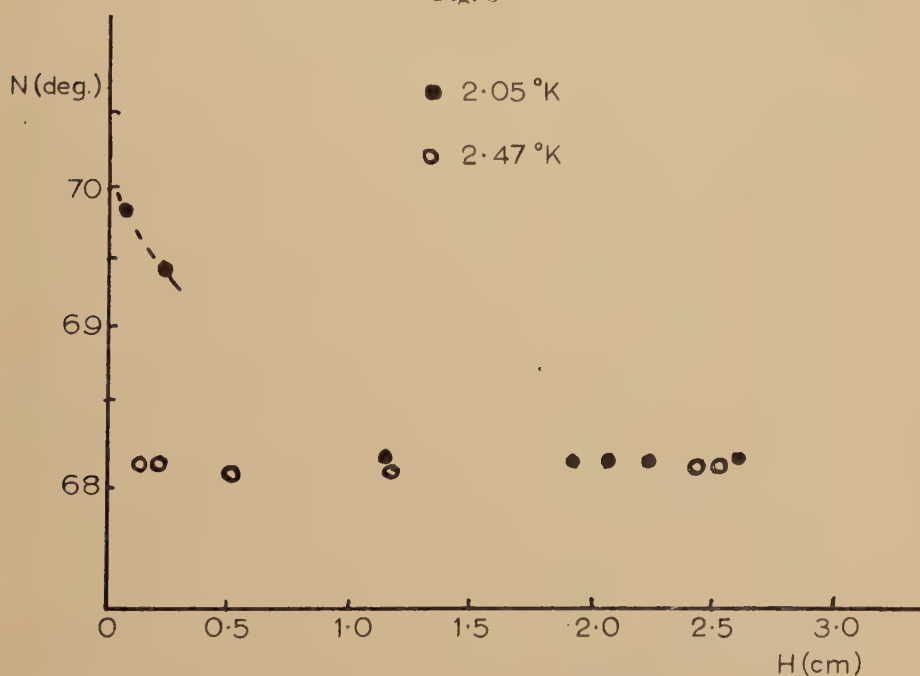
but the final figures are not yet available.

For a comparison with theoretical expressions for the film thickness it would be desirable to avoid the presence of the barium stearate layers and measure the thickness on various clean pure metal surfaces. It would then be more readily possible to determine whether the film thickness shows the small changes on different metals as predicted by

Schiff (1941) or Franchetti (1957) as a consequence of the somewhat different values of the Van der Waals force constant. This could be done by the microbalance method or a variation of the optical method. Preliminary work has been carried out recently at Bristol in which the visual determinations have been replaced by an electronic method which promises to provide the necessary accuracy. The method and some provisional results have been described by White (1958).

A preliminary account of the determination of the film thickness on a mirror of stainless steel for heights from 2 to 38 cm, using the optical method with electronic registration, has been given by Anderson *et al.* (1957) but no details are yet available.

Fig. 3



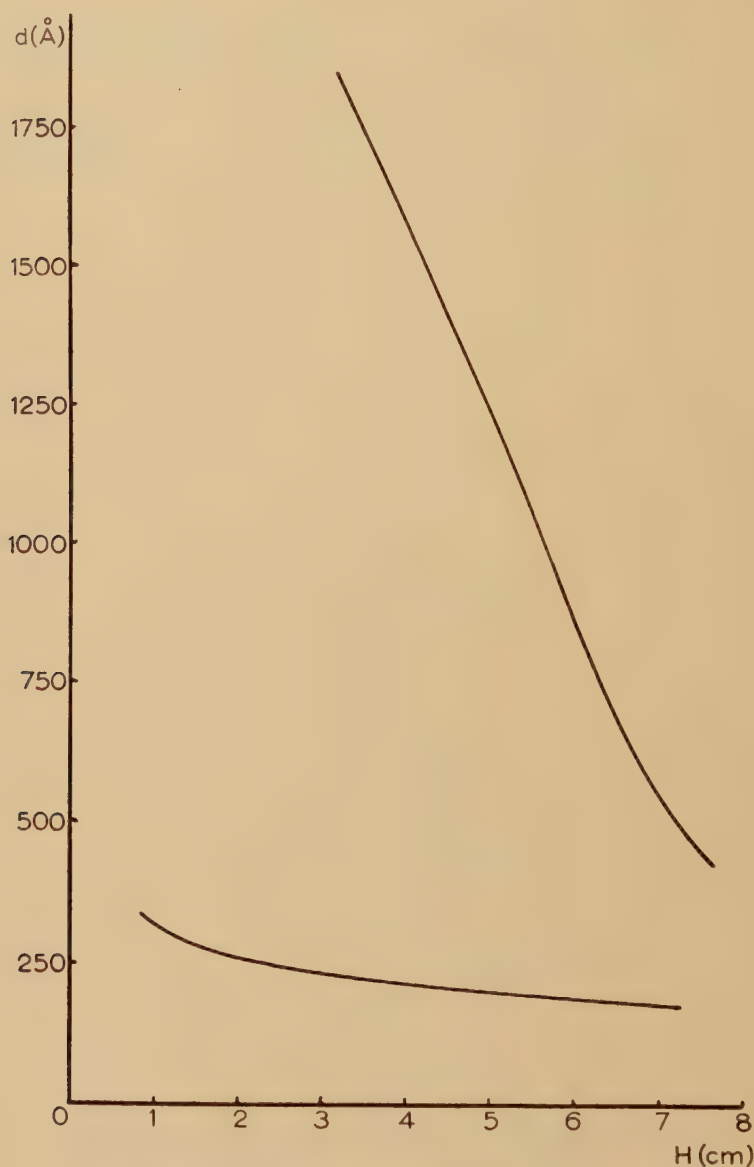
Film formed from the vapour phase.

The helium film may be regarded as an adsorbed film in equilibrium with the vapour in contact with it, Rice and Widom (1953), Atkins (1954), Meyer (1955). The variation of film thickness with height is then due to the gravitational variation of vapour pressure with height. This view leads to the same expression as the Schiff treatment of the problem,  $d = k/H^{1/3}$  and a film should be formed from the vapour phase with the same thickness and profile as in the case where the substrate is in contact with the liquid phase. To test this a small stainless steel mirror was suspended in the gas phase above liquid helium II by attaching it to a



small permanent magnet floating above a superconducting lead dish, Jackson and Grimes (1957). Films formed from the vapour phase were observed with a thickness and profile given in fig. 3. It will be seen that

Fig. 4



Effect of contamination on thickness of He II film.

the variation of thickness with height was much less than when the substrate was in contact with the liquid and the film could form by superfluid flow. The profile was, however, in close agreement with that

expected if the temperature of the substrate was  $10^{-4}$  deg higher than the bulk liquid (see page 453). Evidence was available that the temperature difference was, indeed, of this order of magnitude. When the liquid level was raised to make contact with the floating mirror the observed film thickness had its normal value (first two points of fig. 3).

Kontorovich (1956) and Arkhipov (1957) have shown that a moving film of helium II should be somewhat thinner (a few per cent) than the corresponding static film. A recent repetition by Jackson and Grimes (1958) of the observations of Jackson and Henshaw (1950) on the thickness of the film on the outside of a beaker emptying by film transfer† has shown that the effect does indeed exist. Details will be published shortly.

An example of the influence of contamination of the substrate by condensed impurities on the thickness of the helium II film is given in fig. 4, Jackson and Grimes (1957). The lower curve is the normal  $d$ - $H$  curve for a clean surface and the upper curve for the case when the helium gas admitted to the cold mirror chamber contained about 1 part in 1000 of air as impurity. It will be seen that the thickness is much greater on the contaminated surface. These increased thicknesses may be compared with the increased transfer rates observed by Bowers and Mendelssohn (1949, 1950) on deliberately contaminated surfaces.

It will be seen that owing to the experimental difficulties there was a complete lack of consistency in the earlier determinations of the thickness of the helium II film. As the work progressed the sensitivity of the film to surface contamination, to extraneous radiation, to heat influx and to temperature inhomogeneity was gradually realized and a better approximation to ideal conditions was achieved. It is believed that the most recent work on the helium II film gives a reasonably good approximation to the thickness to be expected theoretically under ideal conditions. This cannot, however, yet be said for the film observed in the helium I region.

#### § 4. HELIUM I FILMS

Theories of helium film formation which attribute the existence of the film to Van der Waals forces, Frenkel (1940) and Schiff (1941), would not predict any change of the film thickness on passing through the  $\lambda$ -point under ideal experimental conditions. In the later theory by Franchetti (1956, 1957) the film thickness is expected to increase steadily with increasing temperature and not to show any discontinuity at the  $\lambda$ -point. However, both Frenkel and Schiff have pointed out that if the experimental conditions permit an appreciable heat influx, any film observed with helium I will be of much smaller thickness than with helium II. On account of its high mobility a helium II film can establish its equilibrium thickness very quickly and replenish itself readily except just below the

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† The accuracy of the earlier observations (at most 5%) was not sufficient for the detection of the small effect predicted by the formula of Kontorovich.

$\lambda$ -point where the transfer rate is small. This cannot, however, occur above the  $\lambda$ -point. Again, Meyer (1954) has pointed out that a very small reduction of the helium vapour pressure below the saturation value causes a large reduction in the thickness of the film. A subsequent increase to the saturation value at temperatures above the  $\lambda$ -point will only lead to a slow build-up to the original thickness of the film owing to the lack of superfluidity and the low thermal conductivity preventing the rapid removal of the heat of condensation.

All the earlier observations of the film above the  $\lambda$ -point have indeed produced values for the thickness which are much smaller than those observed below the  $\lambda$ -point. Thus Daunt and Mendelssohn (1939) record that in their investigations the film thickness above the  $\lambda$ -point was less than  $10^{-7}$  cm.

Burge and Jackson (1951) using their optical method observed that the thickness of the helium film fell considerably in the last 0.005 deg below the  $\lambda$ -point. They were not able to quote a value for the thickness above the  $\lambda$ -point as what they determined in these initial observations was the difference between the thickness of the film at some temperature in the helium II region and that a few tenths of a degree above the  $\lambda$ -point. Jackson and Henshaw (1950) using the same method, brought an infra-red source close to the cryostat and "burned off" the film just above the  $\lambda$ -point. The thickness of the film present under their experimental conditions proved to be about 10 atomic layers at about 2.3°K. Bowers (1953b), using a microbalance to weigh the film, observed the thickness of the helium II film fell rapidly within a few thousandths of a degree below the  $\lambda$ -point and that the thickness above it was about  $4 \times 10^{-7}$  cm, i.e. 10–11 atomic layers. He also noticed that the thickness of the film was very sensitive to radiation influx.

The observations on the helium II film by Ham and Jackson (1957) under greatly improved conditions of temperature uniformity and freedom from extraneous heat influx were extended to the helium I region. After some preliminary tests it was found possible to produce films of considerable thickness (80–90% of that at 2.05°K) which were stable and repeatable. At some temperature above the  $\lambda$ -point (2.47, 3.00, 3.41, 3.82°K) helium was condensed into the mirror chamber. A thick uneven film was observed† which spread only very slowly. If a 6-watt lamp was brought near the cryostat the film evaporated. On removing the lamp the film reformed uniformly and attained its maximum thickness in about 1 minute and remained of constant thickness for the next 30 minutes. This film could be again evaporated and reformed exactly as stated above.

The sensitivity of the film thickness above the  $\lambda$ -point to extraneous radiation was also shown by the fact that the film evaporated almost completely in about 10 minutes when the room lights were switched on.

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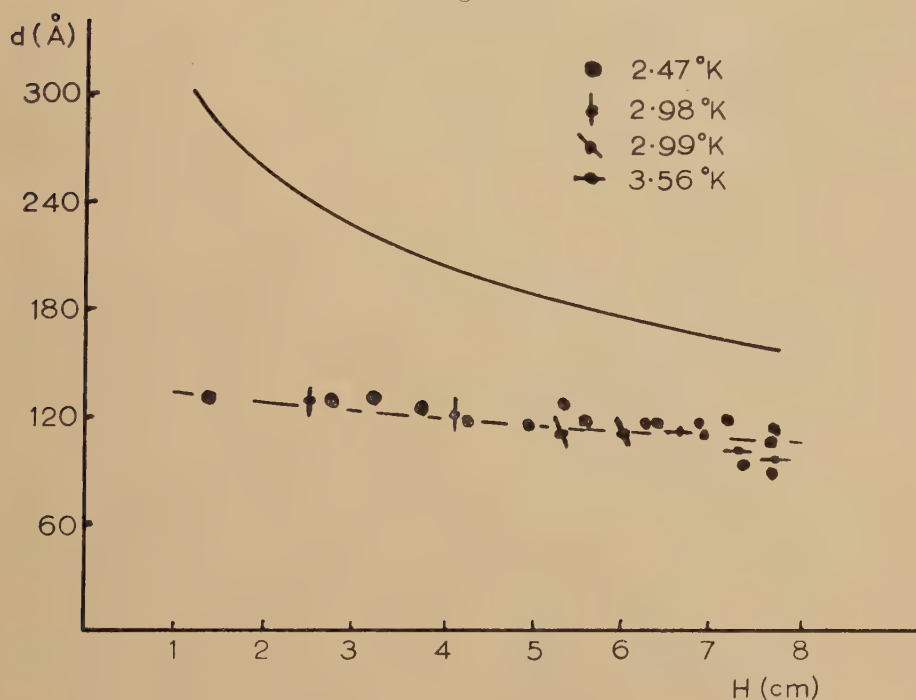
† Except at temperatures near the  $\lambda$ -point where the film was more uniform in thickness.



These observations have been extended by Jackson and Grimes (1957) and the results are shown in fig. 5. The full curve gives the observed thickness of the helium II film at  $2.05^{\circ}\text{K}$  as a function of height above the liquid surface to compare with the dotted curve which gives the thickness for various temperatures above the  $\lambda$ -point. It will be seen that the helium I observations all fall fairly well on the same curve and that the thickness varies very much less with height than in the helium II film.

Figure 3 shows a similar set of observations above the  $\lambda$ -point but made with the 'floating mirror' so that the mirror was in contact only with helium vapour. A thick film was again observed but with a still smaller variation of thickness with height.

Fig. 5



He I film.

The reason for the shape of the helium I curves becomes apparent when the effect of a small increase in temperature of the substrate over that of the bath is considered. Atkins (1954) and Meyer (1955) have shown that an increase of temperature of  $\Delta T$  is equivalent to an increase of  $H$  by  $\Delta H$  in the isothermal case where  $\Delta H$  is proportional to  $\Delta T$ , see p. 453 and fig. 7. A fortunate but unexpected circumstance made it possible to form a reasonable estimate of the value of  $\Delta T$  for the floating mirror at temperatures above the  $\lambda$ -point such that  $\Delta T = 10^{-4}$  deg. Comparison of the observed curve in fig. 3 and the curve for  $\Delta T = 10^{-4}$  deg

in fig. 7 shows that there is a close agreement between the two curves. On this basis it might be reasonable to expect  $\Delta T$  for the long mirror in contact with liquid helium I would be about  $5 \times 10^{-5}$  deg. The shape and position of the curve in fig. 5 agree well with the corresponding curve of fig. 7.

It thus seems likely that, under ideal conditions, the film is of comparable thickness above and below the  $\lambda$ -point as is also expected from measurement of the adsorption isotherms (Long and Meyer 1953). The present results are not in contradiction with the observations of Brewer and Mendelssohn (1953) of a jump in thickness of the film at the  $\lambda$ -point provided the absolute value of the jump does not increase much in going from 95% to 100% saturation.

It is, however, unlikely that the observed values of the thickness of the helium I film will ever be strictly comparable with theoretical predictions of the value under ideal conditions.

Allowances must always be made for the effect of small deviations from ideal conditions and the amount of the deviation can hardly be estimated with precision.

#### § 5. THEORIES OF THE FORMATION AND PROFILE OF THE HELIUM FILM

Frenkel (1940) and Schiff (1941) have put forward theories in which the formation of the helium film is attributed to the van der Waals forces between the helium atoms and the substrate and between the helium atoms in the film. The equilibrium thickness of the film at any height  $H$  is obtained by minimizing the sum of the van der Waals potential energy and the gravitational potential energy of an atom at the surface of the film. As the potential energy of the van der Waals attraction between two atoms varies as the inverse sixth power of the distance, this, when integrated over the semi-infinite vertical wall of the substrate, leads to the formula

$$d = k/H^{1/3}$$

where  $k$  is a constant, which has the following values according to Schiff: copper,  $4.3 \times 10^{-6}$ ; silver,  $4.7 \times 10^{-6}$ ; glass,  $4 \times 10^{-6}$ ; rock salt,  $2.2 \times 10^{-6}$ . It will be seen that the formula gives predictions of the order of magnitude of the observed thickness and the height variation. No suggestion is made of any possible variation of thickness with temperature. No systematic investigation has yet been made of the variation of film thickness with variation of the nature of the substrate. At the time the theories were put forward the observed thickness of the film in the He I region was very small compared with that in the He II region and both Frenkel and Schiff attribute the difference to the presence of a heat influx into the film. In the case of He II the loss due to evaporation can be replenished rapidly by superfluid flow but this is not possible with He I. In the ideal isothermal case the film should on these theories have the same thickness and profile in the He I and He II regions,

Byl *et al.* (1941) attribute the thick film in He II not to van der Waals' forces but to a zero-point energy possessed by atoms in the film. They take an ideal Bose-Einstein gas as the model for the helium in the film with a ground state wave function of the type  $\psi = A \sin(\pi x/d)$  with a node at the wall and the surface of the film. The zero-point energy per atom is then  $\hbar^2/8md^2$  ( $m$  = mass of helium atom) and this must be added to the gravitational energy  $mgH$  to give the total energy per atom. The total energy per  $\text{cm}^2$  of film is proportional to the thickness  $d$  and minimizing this total energy gives

$$mgH - \frac{\hbar^2}{8md^2} = 0$$

$$d = \hbar/m(8gH)^{1/2} \approx 10^{-5} H^{-1/2}.$$

This expression is in agreement with the observations of Bowers (1953 b) both as regards the value of the constant and the variation of thickness with height but not with those of any other observer. At any temperature above the  $\lambda$ -point, i.e. above the Bose-Einstein condensation temperature according to the theoretical basis of the theory, the film thickness should be drastically thinner than it is in the He II region.

The theory has, however, been criticized severely. In the first place the total energy of the film tends to infinity as  $d$  tends to zero. Secondly, Mott (1949) has pointed out the improbability of the assumed ground state wave function which requires the density of the helium in the film to be a maximum at the centre and fall off to zero at the surface and at the wall. The ideal Bose-Einstein gas model implies that interactions between the helium atoms have been neglected but an inclusion of them in the theory completely alters the form of the ground state wave function and the film thickness is no longer inversely proportional to the square root of the height. Atkins (1954) has shown the importance of the existence in the film of a zero-point energy appreciably different from that in the bulk liquid. As a first step to a more complete solution he calculates the zero-point energy of the atoms in the film due to the longitudinal Debye modes of vibration and finds for a slab of thickness  $d$ , the zero-point energy  $Z$  given by

$$Z = Z_{\infty} \left[ 1 - \frac{1}{6} \frac{\lambda_c^{\infty}}{d} + \frac{1}{32} \left( \frac{\lambda_c^{\infty}}{d} \right)^2 + \dots \right]$$

where  $Z_{\infty}$  is the zero-point energy of the bulk liquid and  $\lambda_c^{\infty}$  is the cut-off wavelength of the normal modes in the bulk liquid. The total energy is then the sum of the above  $Z$ , the van der Waals energy and the gravitational energy. Minimizing the total gives the following expression for the film thickness  $d$  at height  $H$ .

$$gH = \frac{\alpha}{d^3} + \left( \frac{\lambda_c^{\infty}}{d} \right)^2 \left[ \frac{1}{32} Z_{\infty} - \frac{1}{72} K \rho Z_{\infty}^2 \left( 1 + \frac{\rho}{c} \frac{dc}{d\rho} \right)^2 \right]$$

where the first term on the right-hand side represents the van der Waals term of the Frenkel-Schiff theory and  $K$  is the compressibility of liquid



helium and  $c$  the velocity of first sound. As mentioned on p. 442 the observations of Ham and Jackson (1957) can be represented over a restricted range of height by an expression of the form

$$H = \left(\frac{A}{d}\right)^3 + \left(\frac{B}{d}\right)^2$$

as suggested above with  $A$  and  $B$  of the same order of magnitude.

According to Franchetti (1956, 1957) the profile of the helium film  $d = d(H, T)$  is determined by the condition

$$\frac{\partial}{\partial d} \Delta F(H, d) = 0$$

with  $\Delta F = F_{\text{film}} - F_{\text{bulk}}$  where  $F_{\text{film}}$  is the free energy per  $\text{cm}^2$  of the film at a given height  $H$ , and  $F_{\text{bulk}}$  is the free energy of the same amount of helium in the bulk liquid.  $\Delta F$  is written as the sum of four contributions

$$\Delta F = \Delta F_w + \Delta W_g + \Delta E_0 + (\Delta F)_{\text{exc}}$$

where  $\Delta F_w$  is the difference in free energy due to the van der Waals forces,  $\Delta W_g$  the gravitational energy per  $\text{cm}^2$  of the film,  $\Delta E_0$  the difference in zero point energy between the helium present in  $1 \text{ cm}^2$  of the film (at height  $H$ ) and the same amount of helium in the bulk liquid,  $(\Delta F)_{\text{exc}}$  the contribution to  $\Delta F$  due to the 'exciton gases' present in liquid helium. The various terms are calculated by Franchetti, the latter two terms involving effects due to the smallness of the film thickness.  $\Delta E_0$  being similar to the zero-point term calculated by Atkins. The main results of the theory are summarized by Franchetti as follows:

(1) The form of the film is determined by a delicate balance between several small effects, among which there are 'limitation' effects on the thermodynamic functions due to the smallness of the thickness.

(2) The temperature dependent properties of the static film are essentially due to 'limitation' effects on excitons, the main contribution coming from 'quadratic' excitons.

(3) The thickness of the static film at a given height above the surface of the bulk liquid increases with temperature for temperatures below the  $\lambda$ -point. This effect should be somewhat greater for a metal wall than for a stearate-coated one. Above  $T_\lambda$  the situation is more uncertain but, presumably, the thickness of the film should reach a maximum and then decay with increasing temperature although it is very likely that the critical temperature is reached before the film has faded away.

(4) Representing the thickness of the static film as  $d = d_0 H^{-1/z}$  the value of  $z$  is between 2 and 3. It increases with height and decreases slightly with increasing temperature.

(5) The value of  $z$  (at a given height and temperature) depends on the nature of the wall. Walls exerting stronger Van der Waals attractions should give  $z$  values nearer to 3. (Qualitatively  $z_{\text{metal}} > z_{\text{glass}} > z_{\text{paraffin}}$ .)

The calculated thicknesses of the film as a function of temperature and height for a barium stearate-coated wall (to compare with the observations

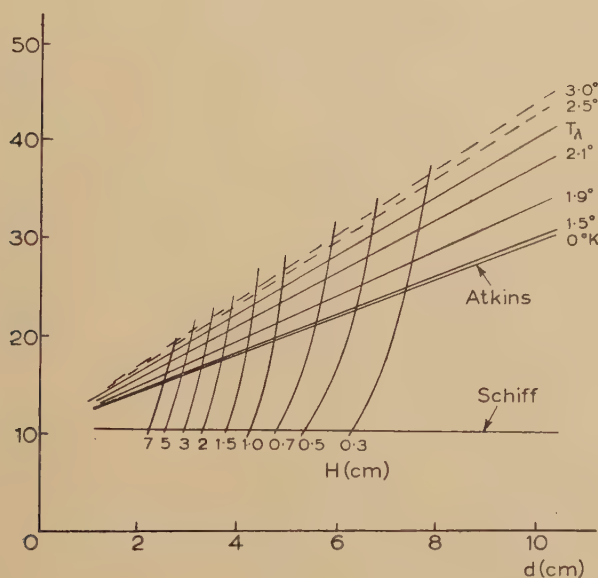
of Ham and Jackson (1957) and Jackson and Grimes (1957)) are shown in fig. 6. The general agreement with the experimental values is good but the calculated thicknesses are larger than the observed ones ( $5.6 \times 10^{-6}$  cm at  $T = 2.0^\circ\text{K}$  and  $H = 1$  cm in place of  $3.15 \times 10^{-6}$  cm).

McCrum and Eisenstein (1955) have considered the change in the Frenkel-Schiff formula which would result from the presence of an electrostatic field at the surface of the substrate, such as might occur with metal surfaces or with surfaces covered by an irregular deposit of polar impurity. The thickness  $d$  of the film is then given by

$$d = [k / (MgH - \frac{1}{2}N\alpha E^2)]^{1/3}$$

where  $k$  is a constant depending on the van der Waals interaction of a

Fig. 6



Franchetti's curves for film thickness on a stearate-coated substrate. The thickness is given by the abscissa of the intersection of the straight line labelled according to  $T$  and the parabolic curve labelled according to  $H$ .

helium atom with a wall atom,  $M$  the g mol weight of helium,  $N$  Avogadro's number,  $\alpha$  the polarizability of helium. Inserting  $\alpha = 2.10 \times 10^{-25}$  and  $k = 26 \times 10^{-14}$  the film thickness at 1 cm height is found to be increased by 7% for  $E = 100$  e.s.u. and 40% for  $E = 200$  e.s.u. Since the field is likely to be very large locally for an irregular deposit of impurity on the plane substrate, it would be expected that the film thickness for a contaminated surface would be much larger than for a clean surface in agreement with observation on He II. As, however, the anomalously thick film does not exist in the He I region according to the observations of Ham and Jackson (1957) the problem is not fully resolved.

The film exists in the field of force of the very large van der Waals attraction. Consequently there is an increase of pressure and of density across the film from the outer surface towards the substrate. This variation of pressure and density has been calculated by Atkins (1954) and Franchetti (1956). The result of the calculations is that the first two atomic layers nearest the wall must be considered as solid and that at temperatures just below the  $\lambda$ -point the pressure in the next layers is above the  $\lambda$ -curve and consequently there are three regions in the cross section of the film (1) solid, (2) He I, (3) He II, proceeding outward from the wall. The outermost layers are of smaller than average density.

The Frankel-Schiff formula has been derived in another way which underlines a different aspect of the problem (Rice and Widom 1953, Atkins 1954, Meyer 1955). The helium film is considered as an adsorbed layer in equilibrium with a very slightly unsaturated vapour. At a height  $H$  above the bulk liquid the pressure  $p$  in the vapour is given by

$$H = - \frac{RT}{mg} \ln \left( \frac{p}{p_0} \right)$$

where  $p_0$  is the saturated vapour pressure at temperature  $T$ ,  $m$  the molecular weight of helium and  $R$  the gas constant. Consequently, if the form of the adsorption isotherm very close to saturation were known, the variation of thickness with height of the 'saturated' film in contact with bulk liquid could be determined from the above equation. Theoretical considerations (Frenkel 1946, Halsey 1948, Hill 1946, 1947, McMillan and Teller 1951, Bowers 1953a) have shown that at high saturations the isotherm should have the form

$$\ln \left( \frac{p}{p_0} \right) = \frac{K}{d^3}$$

where  $d$  is the thickness of the adsorbed layer and  $K$  is a constant. Combining these equations gives the variation of 'saturated' film thickness with height in the form

$$d = k/H^{1/3}$$

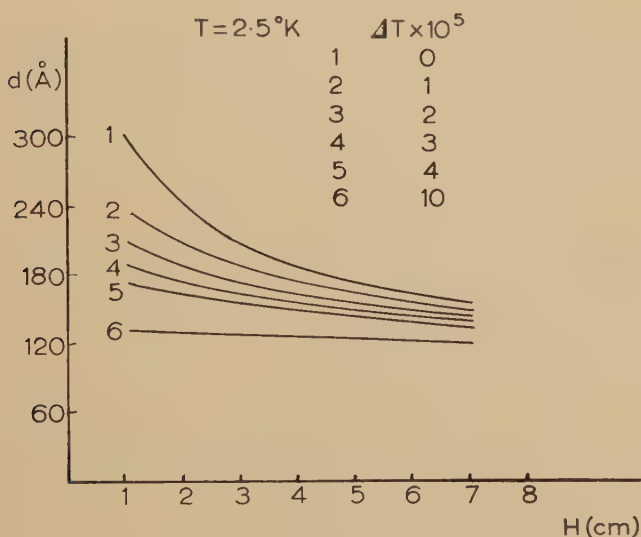
where  $k = -(RTK/mg)^{1/3}$ . This method of deriving the formula suggests that the profile and thickness of the 'saturated' film should, for the strictly isothermal case, be the same whether the substrate is in contact with the bulk liquid or not (apart from edge effects where the curvature of the substrate changes rapidly, Meyer (1955)). This conclusion has been tested experimentally by Jackson and Grimes (1957), see p. 444.

In a comparison of experimentally observed thicknesses of the helium film with theoretical estimates it is of interest to know the effect of the substrate being at a slightly higher temperature than the bulk liquid, either by absorption of radiation or conduction of heat from above. It is not anticipated that this effect will be of importance in an adequately shielded substrate in contact with liquid He II as any temporary temperature difference will produce a superfluid flow by the fountain



effect†, replenishing any evaporated helium in the film and reducing the temperature difference below  $10^{-6}$  deg. Such effects can, of course, be produced and observed, by deliberate production of a large heat influx. However, for a substrate in contact only with liquid He I or with the vapour above liquid He II, a temperature difference may well exist and is in practice extremely difficult to avoid. The importance of such a temperature difference can be shown as follows. Consider the substrate and the film on it to take up a temperature  $T_1$  which is slightly higher than the temperature  $T$  of the bulk liquid so that  $T_1 = T + \Delta T$ . The vapour pressure at a height  $H$  will be given by  $V(T) \exp(-mgH/RT)$  and the saturated vapour pressure of the film at that point will be  $V(T_1)$ .

Fig. 7



Effect of  $\Delta T$  on film thickness.

Consequently the equilibrium thickness  $d$  of the film will be given by

$$d^3 = K / \ln \left( \frac{V(T) \exp(-mgH/RT)}{V(T_1)} \right).$$

Since  $\Delta T$  is small, we have

$$\ln V(T_1) = \ln V(T) + \frac{\Delta T}{V} \cdot \frac{dV}{dT}$$

and hence

$$d^3 = K / \left[ -\frac{mg}{RT} \left( H + \frac{RT}{mg} \frac{\Delta T}{V} \frac{dV}{dT} \right) \right].$$

† As Atkins (1957 a) points out, a temperature gradient of  $10^{-4}$  deg/cm is adequate at  $2.0^\circ\text{K}$  to counteract gravity.

Thus the thickness of the film at height  $H$  and temperature  $T + \Delta T$  corresponds to that at height  $H + (RT/mg)(\Delta T/V)(dV/dT)$  and temperature  $T$ . Inserting the numerical values for  $3.0^\circ\text{K}$ , a  $\Delta T$  of  $10^{-5}$  deg corresponds to an increase of height of 1 cm. Figure 7 shows the effect for various values of  $\Delta T$  and shows that quite small values of this quantity are capable of greatly reducing the observed film thickness and of changing its profile considerably.

All discussion so far has concerned the static helium film. The problem of the thickness of a film on the outside of a vessel emptying by film transfer has been considered by Kontorovich (1956). To allow of the motion of the film he adds a term  $-(\rho_s/2\rho)v_s^2$  to the chemical potential of the helium per unit mass and derives the following formula for the thickness of the film

$$d = \left( \frac{\alpha}{gH} \right)^{1/3} (1 - q)$$

where  $q = (\rho/6\rho_s)(Q^2/\alpha)(\alpha/gH)^{1/3}$ ,  $Q$  = transfer rate in  $\text{cm}^3/\text{cm sec}$ ,  $\alpha$  = van der Waals constant of the Frenkel-Schiff theory. The formula indicates that the moving film should be thinner than the static film by a few per cent. A similar result has been derived by Arkhipov (1957).

## § 6. FILM TRANSFER RATES

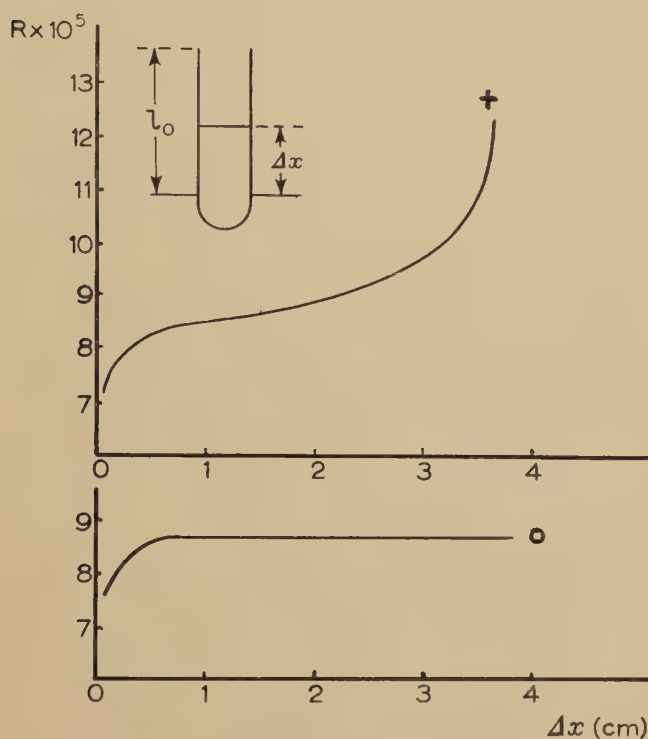
The investigations of Daunt and Mendelssohn (1939) on the transfer of liquid helium II into or out of glass beakers taking place through the helium film under isothermal conditions led them to the following conclusions:

Under isothermal conditions liquid helium II always collects at the lowest available level. The rate of transfer is (1) almost independent of the difference in height between the liquid levels, (2) independent of the length of the connecting film, (3) independent of the material of the substrate, (4) proportional to the smallest perimeter of the connecting surface above the upper liquid level, (5) a function of the temperature. The transfer rate measured in  $\text{cm}^3$  of liquid flowing per cm of the perimeter per sec varies from  $7.5 \times 10^{-5}$  at  $1.1^\circ\text{K}$  to 0 at the  $\lambda$ -point.

The phenomenon was regarded as purely a property of liquid helium II, probably a quantum mechanical property associated with the zero-point energy of the liquid. The existence of a definite transfer rate at any specified temperature was due to the critical velocity of flow of helium II in the film, below which the flow was free from frictional resistance but above which dissipative effects occurred. The critical velocity was reached on the inner surface of the beaker and so the flow on the larger outer surface would be sub-critical and form the simplest example of pure superfluid, resistanceless flow. The critical velocity was believed to be independent of the temperature and the variation in transfer rate with temperature due to the variation of the proportion of superfluid in the film. Thus the curve of transfer rate against temperature should reproduce the  $\rho_s/\rho - T$  curve.

The observations of Daunt and Mendelssohn were repeated and extended by many workers after the war with very varied results. Some of the observations with glass beakers, Webber *et al.* (1949), Fairbank and Lane (1949), Burge and Jackson (1950) agreed either very well or reasonably well with the earlier work, but on the other hand the observations of Atkins (1948) and de Haas and van den Berg (1949) gave transfer rates which were much higher than those of Daunt and Mendelssohn and which varied considerably with the difference in height of the liquid levels.

Fig. 8



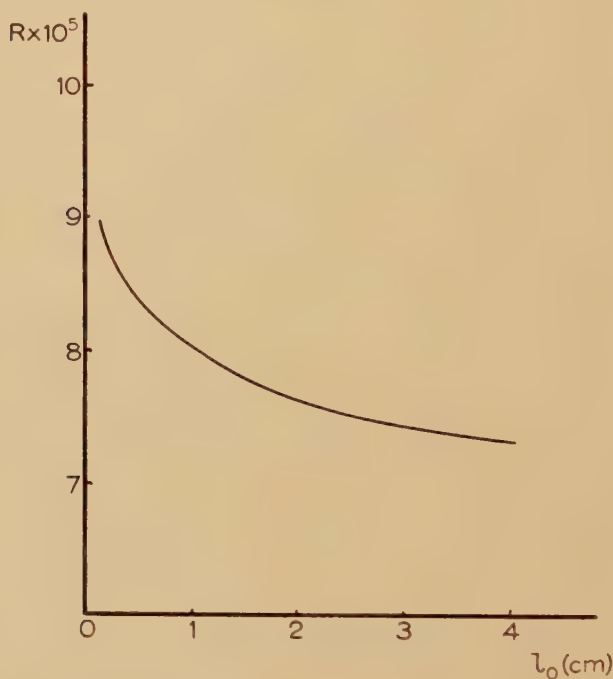
Dependence of the rate of transfer on the level difference,  
 + emptying,  $l_0 = 3.78$  cm ; O, filling,  $l_0 = 0.82$  cm.

The reason for the discrepancy was apparent when Bowers and Mendelssohn (1950) investigated the transfer rate in glass beakers contaminated with a layer of solid air, hydrogen or neon. Even when the impurity was so small that the solid deposit was quite invisible, the transfer rate was increased by a factor of up to ten times. The large variation of transfer rate with position of the liquid levels was also found to be explained by the degree of contamination of the glass surface being greatest at the rim of the beaker and decreasing downwards. The actual



mechanism for the increase of transfer rate is still not known with any certainty and would repay more detailed investigation. The solid deposits are certainly granular or acicular and so one factor will be an increased perimeter presented to the film, but in view of Smith and Boorse's (1955) discussion of the situation this is unlikely to be the complete solution of the problem. Other factors are the changed nature of the surface which may result in an appreciably different van der Waals attraction between the helium atoms and the substrate and there may be an effect due to electrostatic forces in the irregular deposit as suggested by McCrum and

Fig. 9



Variation of filling rate with height of the film. Temperature  $1.47^\circ\text{K}$ .

Eisenstein (1955). Bowers and Mendelssohn's observations emphasized the need for utmost 'cleanliness' in all work on the helium film and later work was in general much more consistent.

The later observations of Atkins (1950 b) and Eselson and Lasarew (1952) carried out under 'clean' conditions with glass beakers, gave transfer rates closely similar to the then accepted values but drew attention to the variations of transfer rate with height which had been regarded by Daunt and Mendelssohn as secondary features outside the principal phenomenon. Atkins' observations are reproduced in figs. 8 and 9.

It will be seen that the emptying curve has the characteristic S-shape found by other observers, the approximately constant middle portion being larger the longer the beaker. On the other hand, the filling rate is constant except when the level difference is less than 0.5 cm. Figure 9 shows the variation of the filling rate with the height of the rim of the beaker above the bath level. As Atkins points out, these observations can be correlated if it is assumed that the important factor in the transfer rate is the height of the rim of the beaker above the higher of the two liquid levels. During filling the bath level is the upper one and remains constant or nearly so during the measurements, whereas during emptying the upper level is the inner one and that changes steadily. As the film thickness varies with height the assumption is that the transfer rate depends in some way on the film thickness. This, of course, implies  $v_c d \neq \text{constant}$ .

The extension of transfer rate measurements to metal beakers did not at first result in an improved understanding of the subject, the published results being distinguished by their variety rather than their consistency. Daunt and Mendelssohn in their 1939 paper stated that the transfer rate on polished copper was the same as on glass but that it was much larger on drawn copper wires, probably because of the larger micro-surface produced in the latter by the drawing process. Boorse and Dash (1950, 1951) published a series of measurements on Pyrex glass, stainless steel, lead, cold-rolled steel, machined copper, polished copper, etched copper and etched copper which had been oxidized. While the transfer rate at 1.3°K on Pyrex glass,  $7.6 \times 10^{-5}$  cm<sup>3</sup>/cm sec agreed very well with the data of Daunt and Mendelssohn, the rates at this temperature for the metals were much higher,  $33.3 \times 10^{-5}$  for lead,  $14.8 \times 10^{-5}$  for machined copper,  $23.0 \times 10^{-5}$  for polished copper and  $51.2 \times 10^{-5}$  for etched copper. The results for copper were thus not in the order of the expected roughness of the respective surfaces.

Mendelssohn and White (1950) measured the transfer rate on platinum and nickel. After a preliminary cleaning the metal beakers were heated to 600°C for one hour at a pressure of  $10^{-3}$  mm Hg to degas them. The observed transfer rates at 1.2°K were 3 to 3.5 times as large as the glass rate. Polishing the platinum surface had very little effect on the observed rate.

Chandrasekhar and Mendelssohn (1955) reported transfer rates measured with a thin-walled beaker of stainless steel the outer surface of which had been submitted to a super-polishing process so that the asperities of the surface were not large compared with the thickness of the helium II film. The measured transfer rate was closely similar to that on Pyrex glass, but when the beaker was heated to red heat and then lightly polished the rate was many times as great as before the treatment.

To explain these large transfer rates it was suggested that the metal surfaces presented a larger microperimeter to the film than a glass surface

with the same macroperimeter and that this microperimeter, the 'roughness' of which had to be on a scale large compared with the film thickness to be significant, would vary with the treatment (heating, machining, polishing, etc.), given to the metal. Furthermore, longitudinal cracks might be present or be produced by heating or be freed from readily adsorbed material such as water by heating and in these cracks a liquid flow could occur which was pressure-independent as in the narrowest channels investigated by Allen and Misener (1939). When all these factors had been allowed for the transfer rate might then be the same for all substrates, but it was obvious that at this stage it was by no means certain what this standard transfer rate would be.

In view of the unsatisfactory state of the problem Smith and Boorse in 1955 published a series of four papers in which they first submitted the evidence to a very complete critical review and then investigated in turn the role of the substrate, of the surface finish, of the film height and of the temperature, obtaining sufficiently complete data in each case for them to have statistical significance. The reader is recommended to read this series of papers as they are still the most complete and accurate account of transfer rate measurements. The work of Smith and Boorse gives a clear account of the present state of the subject, but it is by no means apparent what the ultimate picture will be.

In these papers the transfer rate was determined electronically by means of a capacitor depth gauge which gave the transfer rate for four different ranges along the height of the beaker. The first work was to establish the degree of reproducibility of the observations. Measurements were made with a beaker after a standard procedure of evacuation, etc., the measurements were repeated on another day, the beaker was then dismantled from the cryostat, remounted later and again measurements made. In this way the background variation of the observed transfer rate was established and showed that only after many observations made in a standard manner could a statistically satisfactory figure be obtained. Measurements were made on Pyrex, quartz, copper, nickel silver, aluminium, nickel, silver, stainless steel and lucite. The transfer rate at  $1.1^\circ\text{K}$  for the inner liquid level between 4.45 and 5.33 cm from the rim,  $R_4$ , varied from  $12.9 \times 10^{-5}$  for nickel to  $8.6 \times 10^{-5}$  for silver, and the overall variation was so small compared with the factor of 3 or more previously observed that the background variation prevented the detection of any systematic effect of the nature of the substrate.

In the second paper an investigation was made of the effect of surface finish on transfer rate. Measurements were made with various metallic beakers, first with the beaker in its initial state, then with the outside superfinished, and finally with both outside and inside superfinished. In addition measurements were made with Pyrex in its initial state and then with the inner surface fine ground and coarse ground. The observations were then discussed in terms of a model of a rough surface in which  $\lambda$  is the mean distance between peaks and  $2\delta$  the total depth of the hollows. Then the microperimeter  $p$  is related to the



macroperimeter  $p_0$  by the expression :

$$p = p_0(1 + 4\delta/\lambda).$$

From a careful search of all the available information on surface finish Smith and Boorse came to the conclusion that the value of  $\lambda/\delta$  is always to be found within the range

$$20 \leq (\lambda/\delta) \leq 200$$

with the higher value representing the smoother surface. Thus the possible microperimeter would be in the range

$$1.02 \leq (p/p_0) \leq 1.20.$$

For the coarse ground Pyrex glass, taking the roughness as given by the size of the abrasive particles, the calculated  $p/p_0$  was 1.06. The experimental value derived from the average increase of transfer rate after grinding was 1.05 and 1.04 for two different cases. In general, it was concluded that the film follows the microperimeter presented to it but that very large microperimeters with  $p/p_0$  as great as 3 or more do not exist and the discrepant observations must be explained some other way. Finally, a discussion is given of the very great difficulty of producing a molecularly clean surface of a known kind on metals or glass by any process of degassing or chemical cleaning.

In paper III the variation of the observed transfer rate with the height of the inner level from the rim of the beaker is given for Pyrex and various metals. The transfer rates  $R_1 \rightarrow R_4$  for four different ranges of height were presented by plotting  $R_n/R_4$  as a function of  $n$ . It was found that these curves were independent of the temperature and almost independent of the metal, ranging from  $R_1/R_4 = 1.5$  to, of course, 1 for  $R_4/R_4$ . The variation of  $R$  with height is quite similar to that observed by Atkins (fig. 9).

In paper IV the variation of transfer rate with temperature was exhibited by plotting the rate  $R$ , averaged over all heights and normalized by dividing by  $R_{(1.1^\circ\text{K})}$ , against the temperature. The data represented 132 curves for metals and 21 for Pyrex and quartz. The points fell excellently on the curve of  $[1 - (T/T_\lambda)^7]/[1 - (1.1/T_\lambda)^7]$ . The form of the curve was chosen because the ratio  $\rho_s/\rho$  had been represented by  $1 - (T/T_\lambda)^\sigma$ . However, to compare  $R$  with  $\rho_s/\rho$  the values for  $\rho_s/\rho(T)/\rho_s/\rho(1.1^\circ)$  were also exhibited on the graph as a function of  $T$ . It was seen that these points fell below the curve mentioned above. On the other hand the values of  $[\rho_s/\rho(T)/\rho_s/\rho(1.1^\circ)]^{1/2}$  fell above the curve†. The only other systematic study of the temperature variation of  $R$  is that of Mendelssohn and White (1950) in which they found that the transfer rate as measured by them for baked Pyrex, nickel and platinum could be represented by  $R = A[1 - (T/T_\lambda)^6]$  and for unbaked Pyrex by  $R = A[1 - (T/T_\lambda)^8]$ .

† The curves for  $R$ ,  $\rho_s/\rho$ ,  $(\rho_s/\rho)^{1/2}$  against  $T$ , of course, all agreed at  $T = 1.1^\circ\text{K}$  as they were normalized at this temperature and at  $T = T_\lambda$  as they all go to zero at the  $\lambda$ -point.

As Smith and Boorse point out, neither theory nor experiment has yet been able to make definitive statements regarding transfer rates. It cannot yet be stated precisely what theory is called upon to explain and the present state of theory is not sufficiently definite to direct the efforts of the experimentalist. The theories of transfer rates are theories leading to the existence of a critical velocity of flow of liquid helium II. These are discussed in § 9 on Critical Velocities. Two different viewpoints lead to the expressions  $v_c d = \text{constant}$  and  $v_c d^{1/2} = \text{constant}$ , whereas the available experimental information lies in between the predictions of the two expressions. The same can be said with regard to the predictions  $R \propto \rho_s / \rho$  and  $R \propto (\rho_s / \rho)^{1/2}$ .

The theoretical work of Dash (1954) which leads to the expressions  $v_c d^{1/2} = \text{constant}$  and  $R \propto (\rho_s / \rho)^{1/2}$  also predicts a variation of transfer rate with height of the form  $R \propto H^{-1/2z}$  where the thickness of the film is given by  $d = kH^{-1/z}$ . The expression gives a variation of the correct order of magnitude but as the appropriate value of  $z$  cannot yet be stated with the necessary precision the formula cannot be tested quantitatively. In Dash's view the film flow is sub-critical for differences in height of the two liquid levels up to 0.3 cm but for greater heights the flow is supercritical and a resistance to flow sets in. The additional flow for these greater heights is, however, only a few per cent of the sub-critical flow as calculated on Dash's model of the production of excitations in liquid helium II.

The recent observations of Jackson and Grimes† on the formation of drops of bulk liquid from the film during the transfer phenomenon can be used to suggest a picture of the variation of transfer rate with height. These observations, which are an extension of those of Jackson and Henshaw (1950), were made by the polarized light technique described elsewhere in this review and, for the emptying of a beaker by film transfer, were as follows. In the initial stage of the emptying process when the inner liquid level is close to the rim of the beaker the transfer rate is high and drops of bulk liquid of diameter 0.1 to 0.3 mm are seen to run down the outside of the beaker with velocities of the order of 1–2 cm/sec. The drops, which start from the rim of the beaker, are initially numerous. They gradually decrease in number as the inner level falls, disappearing altogether when the latter is about 1 cm from the rim. The drops are seen to disappear (re-enter the film, see § 10) at some point above the outer bath level, the height of this point rising as the number of drops diminish. In addition, Jackson and Henshaw's observation that the thickness of the film on the outside of the beaker was independent of the position of the inner liquid level was confirmed.

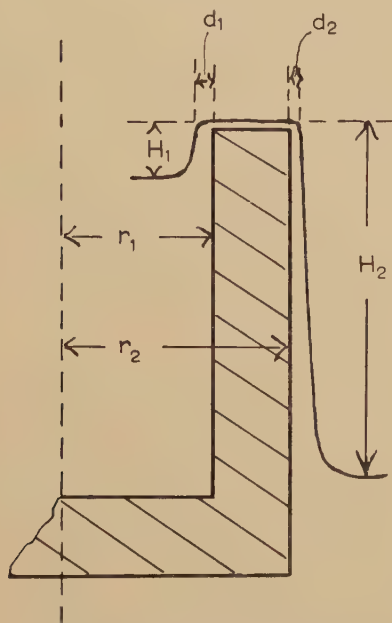
This suggests that the flow is governed by the thickness of the film on the inside of the beaker at the rim where the film is moving with the appropriate critical velocity. Because the film at the rim on the outside

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† To be published shortly.

of the beaker is much thinner the whole of the flow on the outside cannot be carried by true film flow and the excess liquid appeared as drops of bulk liquid. As the inner level falls the difference in film thickness inside and outside becomes less marked and a greater proportion of the flow can be carried by the outer film, the drops diminish in number and finally disappear. The drops slide down the outside of the beaker until they find a place where the outer film is thick enough to carry the whole of the flow and there they re-enter the film. To obtain a roughly quantitative picture let us assume that the film flow is governed by the expression  $v_c d^{1/2} = \text{constant}$  and the film thickness by  $d = kH^{-1/3}$ . Let the inner and outer radii of the beaker be  $r_1$  and  $r_2$  respectively, the thickness of the

Fig. 10



Helium film during emptying.

inner film at height  $H_1$  from the rim be  $d_1$  and that of the outer film at  $H_2$  be  $d_2$  (fig. 10). The film flow per second at the rim on the inside of the beaker is  $2\pi r_1 v_1 d_1$ . To carry this flow in the film on the outside the velocity at the rim would have to be  $v_2' = v_1 d_1 r_1 / d_2 r_2$ . The actual maximum velocity on the outside at the rim is  $v_2 = v_1 d_1^{1/2} / d_2^{1/2}$ . For the beaker used we have  $2r_1 = 4$  mm,  $2r_2 = 5$  mm, the film thickness may be taken as  $d = 3 \times 10^{-6} H^{-1/3}$  so with initially  $H_1 = 0.1$  cm and  $H_2 = 3$  cm we have  $v_2 = 1.76v_1$  and  $v_2' = 2.49v_1$ .

Thus even on the larger perimeter there will be a considerable proportion of the flow carried as bulk liquid. There will, however, be a point at which the outer film is again able to carry the whole flow. For the



conditions given above the drops re-enter the film at a height 0.38 cm above the bath level.

If the initial conditions are  $H_1 = 1$  cm and  $H_2 = 3$  cm it is found that the outer film flow is sub-critical at the rim and the whole flow can be carried by the film.

In principle observations of the variations of transfer rate with height and of the position at which the drops re-enter the film could be used to determine the actual relation between  $v_c$  and  $d$  in place of the approximate formulae used in the above calculation. The available data are, however, not yet sufficiently comprehensive for this to be done.

### § 7. TRANSFER RATE BELOW 1°K

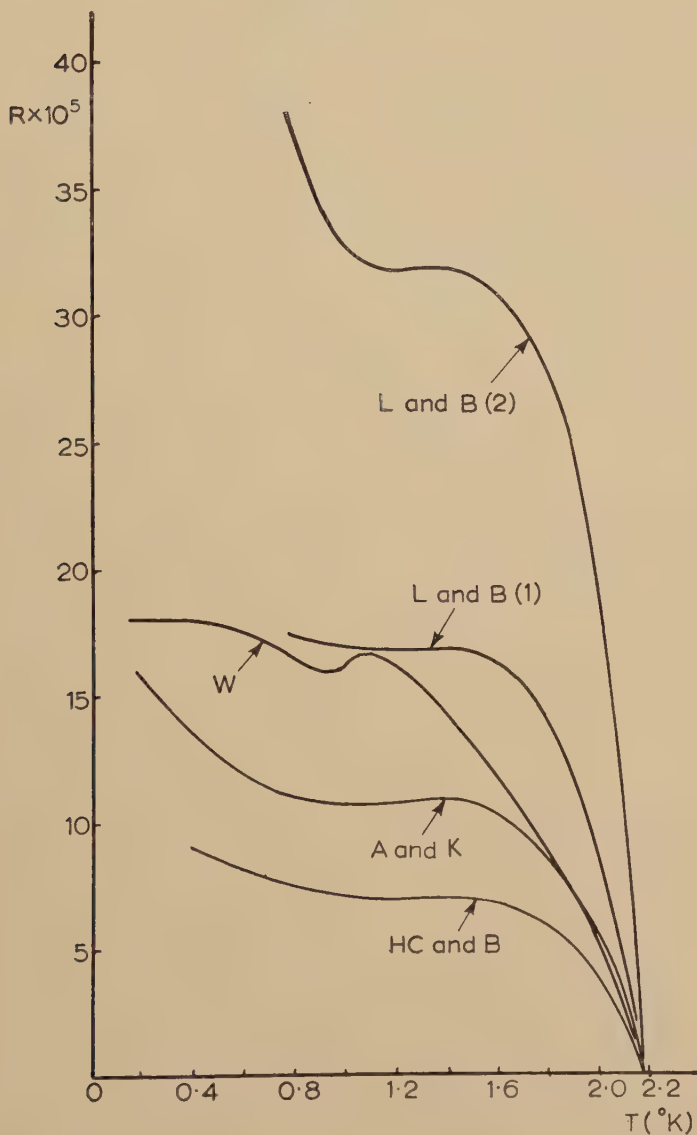
The mass transfer rate through film flow is proportional to the mean velocity of flow, to the thickness of the film and to the fraction of the liquid helium free to move, hence proportional to the superfluid density. If one considers  $v_c d$  to be constant, independent of the temperature, the temperature variation of the transfer rate will be that of  $\rho_s/\rho$ . In particular, it will then be practically constant for all temperatures below, say, 1.2°K. Several investigations have been made in which the measurements have been extended to the temperature range below 1°K. In all cases evidence has been obtained indicating that, after remaining nearly constant from about 1.5°K to 1.0°K the transfer rate increases steadily as the temperature falls below 1°K.

Ambler and Kurti (1952a) have measured the gravity induced transfer rate below 1°K from a glass beaker (type of glass not stated) in which the film flow was limited by a constriction of 1.2 mm diameter. The beaker contained and was surrounded by compressed manganese ammonium sulphate, demagnetization of which cooled the beaker and its contents to 0.14°K. Emptying rates only were measured by the visual observation of the liquid level in the beaker. The warming time from 0.14°K to 1.0°K was about half an hour. Differences up to 15% were observed between different runs and the transfer rates between 1.2°K and the  $\lambda$ -point showed the usual temperature variation but were all higher than the accepted values for a glass surface. It is therefore probable that the freedom from condensed impurities on the glass was not as high as desirable. As apparently shown by Lesensky and Boorse (1952) impurities present may increase not only the absolute value of the transfer rate at any temperature but also the temperature variation of the rate below 1°K. The results of the various runs, normalized to agree at 1.2°K are shown in fig. 11 curve (A and K). It will be seen that the curve is almost flat between 1.2°K and 0.8°K but rises steeply at lower temperatures. The observed rate at 0.2°K is 30% higher than that at 1.2°K.

Lesensky and Boorse (1952) have measured the gravity induced transfer rate from a machined copper beaker in a metal apparatus cooled by the demagnetization of iron ammonium alum or gadolinium sulphate.

Although temperatures as low as  $0.4^{\circ}\text{K}$  could be obtained the rate of warming was too great for any measurements to be made below  $0.75^{\circ}\text{K}$ . The observations were made by the electronic method. Curve [L and

Fig. 11



Transfer rate below  $1^{\circ}\text{K}$ .

B(1)] gives the results for what was believed to be a clean machined copper surface. It will be seen that the curve is flat from about  $1.5^{\circ}\text{K}$  to  $0.9^{\circ}\text{K}$

at about  $17 \times 10^{-5} \text{ cm}^3/\text{sec cm}$  and there is "perhaps a start of a rise at  $0.8^\circ\text{K}$ ". Curve [L and B(2)] where the copper surface was believed to be contaminated shows a flat portion from  $1.3^\circ\text{K}$  to  $1.1^\circ\text{K}$  at the high value of  $32 \times 10^{-5} \text{ cm}^3/\text{sec cm}$  and a rapid rise to about  $38 \times 10^{-5}$  at  $0.75^\circ\text{K}$ .

Gravity induced transfer rates for a Pyrex glass beaker at temperatures below  $1^\circ\text{K}$  have also been made by Hebert *et al.* (1957). A glass capsule containing a small glass beaker and a pill of manganese ammonium sulphate was filled with helium gas to a pressure of 750 p.s.i.g. at room temperature and sealed, taking special precautions to avoid contamination. At the low temperatures the helium condensed and the beaker could be filled by inverting the whole capsule. Temperatures down to  $0.3^\circ\text{K}$  were obtained and the warming time was half an hour. The observed rates of transfer from the  $\lambda$ -point to  $1.0^\circ\text{K}$  agreed well with those of Mendelssohn and White (1950) showing that the beaker was adequately 'clean'. An increase of rate was observed below  $1.0^\circ\text{K}$ , the value at  $0.3^\circ\text{K}$  being 25% greater than that at  $1.0^\circ\text{K}$ , fig. 11, curve (H, C and B).

Waring (1955) has also investigated the transfer rate from  $0.14^\circ\text{K}$  to  $2.17^\circ\text{K}$  using thermally induced film flow. A Pyrex glass beaker was embedded in compressed manganese ammonium sulphate containing a number of copper discs to improve the temperature uniformity. A warming time of two hours was attained. At the upper end of the beaker was a 211 micron capillary which limited the film flow. The film then passed up a vertical thin walled metal capillary and evaporated at the place where the heat influx was adequate. The helium vapour was removed by a fast pump and its volume measured; the narrow metal capillary prevented recondensation of the vapour. Precautions were taken to avoid contamination. The results are shown in fig. 11, curve W. It will be seen that the transfer rates are much higher than those of most of the other observers, rising to  $18 \times 10^{-5} \text{ cm}^3/\text{sec cm}$  at  $0.14^\circ\text{K}$ . The increase from  $1.0^\circ\text{K}$  to  $0.14^\circ\text{K}$  is about 10%. After the low temperature observations the beaker was broken off above the capillary and a gravity induced transfer rate measured at  $1.1^\circ\text{K}$ . Waring states that the observed value ( $12 \times 10^{-5} \text{ cm}^3/\text{sec cm}$ ) "falls within the range of the latest reported rates for gravitational flow over pyrex" but actually it is higher than the majority of determinations. The high transfer rates are suspicious or at best unexplained.

It will be noticed that Waring's transfer rates are constant from  $0.14^\circ\text{K}$  to  $0.5^\circ\text{K}$ . Hebert *et al.* (1957) suggest an explanation of this observation. While the film evaporates, at higher temperatures, at the temperature of the bath liquid, this may not be so at the lowest temperatures and lowest vapour pressures. A kinetic theory calculation shows that liquid carried by the film at the observed flow rate can be evaporated within a few centimetres of the glass capillary only when raised to about  $0.5^\circ\text{K}$ . So with Waring's arrangement a constriction near  $0.5^\circ\text{K}$  would effectively limit flows to that corresponding to this temperature even though the bulk liquid was at a temperature below  $0.5^\circ\text{K}$ .



If the increase of transfer rate below  $1^{\circ}\text{K}$  indicated by all these investigations is taken at its face value it presents a serious theoretical problem. The increase cannot be attributed to  $\rho_s/\rho$  which appears directly or as some power of the ratio in attempts to derive the transfer rate theoretically. Again, views which require  $v_c d = \hbar/2m$  predict a constant creep rate below  $1^{\circ}\text{K}$ . Experimental evidence on film flow between the  $\lambda$ -point and  $1.0^{\circ}\text{K}$  shows that  $v_c d$  is at least approximately constant though allowing for the possibility of some variation with temperature. There is no experimental evidence yet regarding the behaviour of the separate quantities,  $v_c$  and  $d$ , below  $1^{\circ}\text{K}$ . The theoretical work of Franchetti (1957) suggests that the film thickness at a constant height increases steadily from  $0^{\circ}\text{K}$  to the  $\lambda$ -point and the latest experimental evidence, Ham and Jackson (1957) and Jackson and Grimes (1957) from  $1.3^{\circ}\text{K}$  to  $2.16^{\circ}\text{K}$  gives no indication of an increase of thickness below  $1^{\circ}\text{K}$ .

It is, however, very desirable that the determinations of transfer rate below  $1^{\circ}\text{K}$  be repeated under strictly isothermal conditions as all the available work fails to satisfy this very necessary condition to a greater or lesser extent. It is therefore probably better to await confirmation of the, at present, unexpected rise of transfer rate below  $1^{\circ}\text{K}$  before indulging in speculations as to its interpretation.

## § 8. VELOCITY OF FLOW OF LIQUID HELIUM IN THE FILM

It is of interest to know the actual velocity with which the liquid helium moves in the film during a transfer process, more particularly the velocity at the perimeter governing the flow as this can be compared with theoretical estimates of the critical velocity. Such estimates are of significance only when the thickness of the film and the transfer rate are made with the same apparatus and preferably during the same run. These conditions are satisfied in the observations by Jackson and Henshaw (1950) and Atkins (1950 b). A direct measurement of the velocity of advancement of the front of the film spreading over a solid surface has been made by Knudsen and Dillinger (1953, 1954): see also Dillinger (1955). Combination of this velocity with a measurement of the transfer rate gives a value of the average thickness of the film.

Jackson and Henshaw (1950) ground and polished a narrow longitudinal strip of plane mirror on the outside of a cylindrical beaker of stainless steel. The beaker was also provided with a glass capillary tube attached to the bottom of the beaker by a Kovar-glass seal, thus permitting the level of the liquid in the beaker to be observed. It was therefore possible to observe the thickness of the film on the outside of the beaker by the optical method of Burge and Jackson (1951) and simultaneously the transfer rate. It was then possible to calculate the velocity of the film at the point where the thickness was measured. A quantity of greater interest is the critical velocity of the film on the inside of the beaker where the transfer rate is controlled by the inner perimeter. The thicknesses

and transfer rates as measured at various temperatures together with the critical velocities as calculated by Daunt and Smith (1954) are given in table 4. Column 2 gives the observed transfer rate at the temperatures

Table 4

$T$ (°K)	$R$ (cm <sup>3</sup> /sec cm)	$d$ (cm)	$v_{\text{crit}}$ (cm/sec)	$v_{s \text{ (crit)}}$ (cm/sec)
1.1	$16.9 \times 10^{-5}$	$1.63 \times 10^{-6}$	104	105
1.3	16.9	1.63	104	110
1.5	16.8	1.66	101	114
1.7	16.1	1.82	88.5	118
1.9	12.8	1.94	66	118

indicated in column 1, column 3 the thickness of the film on the inside of the beaker at 1 cm above the liquid level, assuming this can be deduced from the observed values on the outside of the beaker, column 4 the critical velocity (on the inside at 1 cm above the inner liquid level), calculated by dividing the transfer rate  $R$  by the thickness  $d$ . This assumes that the whole of the liquid in the film is moving with the same average velocity. If it is supposed, on the other hand, that only the superfluid moves in the film, one obtains column 5 for  $v_{s(\text{crit})}$  by dividing column 4 by  $\rho_s/\rho$ .

If the expression  $dv_c = h/2m$  is combined with a theory of film thickness based purely on van der Waals forces, the values of  $v_{s(\text{crit})}$  should all be the same and equal to about 25 cm/sec. On the other hand, Dash (1954) has derived an expression for the critical velocity of the form  $v_c = 0.087(\alpha\rho_s/\rho)^{1/2}$  where  $\alpha$  is a length associated with the 'clusters' in helium II. The temperature variation of the figures in column 5 is in reasonable agreement with this expression.

The high values of  $v_{s(\text{crit})}$  of column 5 are not to be taken too seriously as they were quoted as provisional ones, due for revision when the provisional calibration of Nicol shift against thickness of film used by Jackson and Henshaw (1950) was replaced by a definitive calibration.

This is now available, and these observations have recently been repeated by Jackson and Grimes (1958) under improved conditions so that the accuracy of observation has been increased considerably. The main purpose of these new observations was to detect the reduction in thickness (a few per cent) of the moving film compared with the static film under the same conditions as predicted by Kontorovich (1956) and Arkhipov (1957). The observations will provide a new table of critical velocities replacing those of table 4. Thus the transfer rate (with the same beaker) is now  $13.4 \times 10^{-5}$  cm<sup>3</sup>/sec cm at 1.60°K, agreeing well with the data of Smith and Boorse (1955 a) and lower than that of Jackson and Henshaw (1950). This was to be expected as special precautions were

taken in the new measurements to avoid contamination of the beaker surface, whereas the serious effect of contamination on transfer rates was unknown at the time of the original measurements. With the new calibration, Ham and Jackson (1957), giving the thickness of the film at 1 cm height and 1.60°K as  $3.02 \times 10^{-6}$  cm, the revised value for  $v_{s \text{ (crit)}}$  at 1.60°K is 54.1 cm/sec.

Atkins (1950 b) has also measured the transfer rate from a glass beaker and then the film thickness in the same beaker from the oscillations about the final level. His results are shown in table 5, calculated by Daunt and Smith (1954) from the graph given by Atkins, temperature 1.47°K. Knudsen and Dillinger (1953) have determined the time for the

Table 5

$R$ cm <sup>3</sup> /sec cm	$d$ cm	$v_{\text{crit}}$ cm/sec
$7.4 \times 10^{-5}$	$1.9 \times 10^{-6}$	39
7.8	2.1	37
8.15	2.3	35

film to spread over a dry surface of copper or stainless steel and assuming the film moves with a reasonably sharp front they deduce an average velocity in both cases of about 37 cm/sec, comparable with the values given by Atkins. Dillinger (1955) records a value of 17.7 cm/sec for the average velocity derived from similar experiments.

## § 9. CRITICAL VELOCITIES IN THE HELIUM II FILM

If the observations of transfer rate are regarded as showing that the essential feature of this phenomenon is that it is independent of the pressure head, so that the observed variations of rate, when the inner level is near the rim of the beaker and when the inner and outer levels are nearly the same, are attributed to special causes and are regarded as of secondary importance, one is led to the conception of a critical rate of flow of the film. Below this critical velocity the flow is entirely free from frictional forces but as soon as this velocity is exceeded dissipation sets in. The flow during film transfer is thus limited by the critical velocity appropriate to the film thickness at the point of observation according to the expression  $dv_c = \text{constant}$ .

Further evidence for frictionless film flow at sub-critical velocities is given by the double beaker experiment (§ 11) and by the observations of Chandrasekhar and Mendelssohn (1955) of film flow induced by a heat input. For small heat inputs the flow through the film into an insulated



volume of liquid helium II, containing an electrical heater is accurately proportional to the heat input up to a certain value of the latter after which a very different type of flow is established.

Theoretical justifications of an expression of the kind  $dv_c = \text{constant}$  have been given by Byl *et al.* (1941) and others. These authors point out that in Daunt and Mendelssohn's experiments the maximum transfer rate is given by  $dv_c = 8 \times 10^{-5} \text{ cm}^2/\text{sec}$  and that this is of the order of magnitude of  $h/2m$  where  $m$  is the mass of the helium atom. They suggest the following picture. As long as the film velocity is smaller than  $v_c$ , the maximum value of the angular momentum  $mrd$  of the surface atoms with respect to the atoms at the wall is smaller than  $h$ . The interaction of these atoms can only take place in 'collisions' with an angular momentum quantum number  $l$  equal to 1. These collisions on the average do not lead to a change of translational momentum: the liquid slips in a state of hydrodynamic potential motion without friction over the wall. When the velocity exceeds the critical value  $v_c = hmd$ , however, collisions with  $l=0$  occur with a larger probability leading to change of momentum, dissipation of energy and friction. The suggestion cannot, however, be formulated in a more precise way in order to give the value of the multiplicative constant, (1/2), in the expression given above.

A similar equation has been derived by London (1945), by Ginsburg (1944, 1949), by Daunt and Mendelssohn (1946 b) and by Mendelssohn (1945).

Franchetti (1955) has also proposed a model leading to a similar critical velocity for the film. He suggests that dissipation will set in when the kinetic energy per atom of the collective adiabatic motion of the helium II reaches a value of the first standing wave having a  $k$  vector perpendicular to the wall ( $\lambda = 2d$ ). This gives

$$(\bar{v}^2)^{1/2}d \simeq 3 \times 10^{-4},$$

and since the velocity field is far from uniform  $v_c < (\bar{v}^2)^{1/2}$ , so that the calculated value of  $dv_c$  may not be much larger than the observed value.

Landau (1941) considered the problem of the production of excitations in bulk helium and the consequent onset of dissipation. He considered the flow will be frictionless until the velocity of the superfluid relative to the walls of the container exceeds a minimum value  $v_c$  given by

$$v_c = \left( \frac{\epsilon(p)}{p} \right)_{\min}$$

where  $\epsilon(p)$  is the energy of the excitation, phonon or roton, and  $p$  its momentum. The critical velocities so calculated are of the order of  $10^4 \text{ cm/sec}$  for both phonons and rotons and are so high compared with the experimental values, which are in the range 30–50 cm/sec, that it may be concluded that any critical velocity limiting film flow cannot be associated with the excitation of phonons or rotons by the mechanism postulated by Landau.

Feynman (1955) has considered the onset of dissipation when liquid helium II flows from a narrow slit into the bulk liquid. He considers that dissipation is produced by the formation of vortices. The critical velocity is defined as that at which the energy is just sufficient to create the vortices, and we then have

$$v_c d = \frac{\hbar}{m} \ln \left( \frac{d}{a} \right)$$

where  $d$  is the width of the slit and  $a$  is a length of the order of the atomic spacing in liquid helium II. If  $d = 10^{-5}$  cm,  $v_c$  is of the order of 100 cm/sec. Assuming that this mechanism is also applicable to film flow, the critical velocity so obtained is not much greater than that observed.

Dash (1954) has modified Landau's picture of the production of excitations by supposing that at the critical velocity the movement of the superfluid produces phonons and that a cluster of moving atoms cooperate in the process. This leads to critical velocities of the observed order of magnitude provided the size of the cluster can be picked appropriately and produces an expression connecting critical velocity and film thickness of the form

$$v_c d^{1/2} = \text{constant.}$$

In Dash's picture the transfer rate is a function of the height of the film and the smaller observed variation is regarded as an essential feature of the phenomenon.

Mott (1949) has suggested a model of helium flow in which part of the superfluid is at rest and part in motion. The tendency for the stationary superfluid 'bubble' to grow at the expense of the flowing superfluid, due to Bernoulli's forces, is counterbalanced by the surface tension at the boundary. When the boundary between the superfluid parts is in equilibrium the velocity is considered to be critical. The model also yields the equation

$$v_c d^{1/2} = \text{constant.}$$

Insofar as the experimental data suggest the existence of a critical velocity, there is a tendency for  $v_c d$  to increase with  $d$  and for the observed values of  $v_c$  to fall in between those calculated from the two expressions,  $v_c d = \text{constant}$  and  $v_c d^{1/2} = \text{constant}$ .

Critical velocities due to the production of other types of excitation have also been considered. Thus Kuper (1956) has considered the excitation of quantized surface waves. He took for the frequency of the wave the expression derived for waves on the surface of deep water in which the governing factors are the surface tension, density and gravitation. With the factors appropriate to liquid helium Kuper calculates a critical velocity for this process of 10 cm/sec and suggests this may be of importance in the case of the helium film. This conclusion has, however, been criticized by Atkins who pointed out that for surface waves on the film the restoring force is not gravity but the Van der Waals' forces

which are much larger than the gravitational force. The critical velocity is then derived from the expression

$$v_c = (3\alpha/d^3)^{1/2}$$

where the van der Waals' force per unit mass is given by  $3\alpha/d^4$ .

Since the equilibrium thickness of the film at height  $h$  is given approximately by

$$\alpha/d^3 \simeq gh$$

we have  $v_c \simeq (3gh)^{1/2} \simeq 50$  cm/sec for  $h = 1$  cm. This expression leads, however, to a variation of  $v_c$  as  $1/d^{3/2}$ , which is not in agreement with the available evidence.

Arkhipov (1957) has also considered the excitation of surface waves on the film. His theory leads to an expression for the critical transfer rate of the form

$$R^2 = \frac{\rho_s}{\rho} \left( \frac{12\alpha\sigma}{\rho} \right)^{1/2}$$

where  $\alpha$  = van der Waals' constant as above and  $\sigma$  is the surface tension. Putting in the observed thickness at 1 cm height ( $3 \times 10^{-6}$  cm) to derive  $\alpha$ , the calculated value of  $R$  becomes  $93 \times 10^{-5}$  cm<sup>3</sup>/cm sec, considerably larger than the observed value.

#### § 10. FORMATION OF BULK LIQUID FROM THE FILM

Daunt and Mendelssohn (1939) first observed the formation of bulk liquid (drops) from the flowing film in the following two cases. The first and obvious case was the formation of drops of helium II at the bottom of a beaker partially filled with liquid and then lifted out of the bath. In the second and less obvious case drops were formed from the film at an intermediate point along its length. Thus when the beaker of fig. 12 was filling with the bath level at B or C and the inner level at A, a small transfer rate, determined by the perimeter of the smaller tubular insert, was observed. If the bath level was at D†, the transfer rate was larger, proportional to the larger inner perimeter at D and drops of liquid were seen to fall from the lower end of the inserted tube.

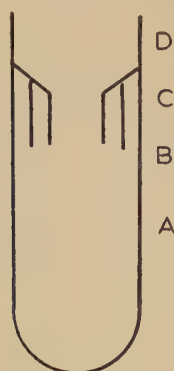
The conditions, under which bulk liquid can be produced from the film, were indicated more clearly by experiments with the beaker shown in fig. 13, Mendelssohn (1951), Chandrasekhar and Mendelssohn (1955), showing the places at which drop formation was observed when the inner liquid level was at the three positions indicated in the figure. From these observations it can be concluded that the transfer rate is (1) governed by the smallest perimeter of the vessel above the higher of the two liquid levels, (2) if the film flows on to a surface, below the higher liquid level, which has a still smaller perimeter, the excess of liquid over that which this smaller perimeter can carry will appear as drops of bulk liquid, and

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Private communication from Dr. K. Mendelssohn,

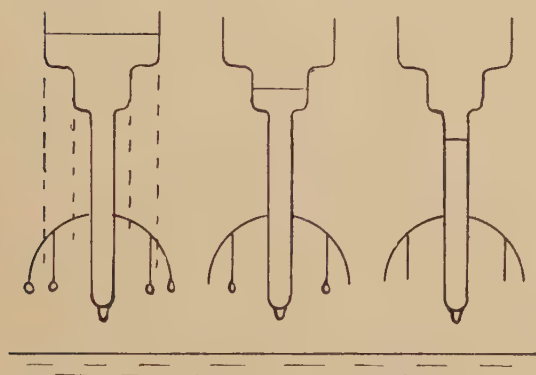


Fig. 12



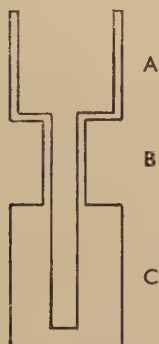
Beaker used by Daunt and Mendelssohn.

Fig. 13



Formation of drops from the film.

Fig. 14



Beaker to show formation of bulk liquid from film,  
Jackson and Henshaw.

(3) if, when bulk liquid has been formed, the latter and the film flow on to a surface of sufficiently large perimeter, the bulk liquid can re-enter the film.

This behaviour has been rendered visible in a series of experiments by Jackson and Henshaw (1953) and Ham and Jackson (1953). A cylindrical beaker of stainless steel having the cross section shown in fig. 14 was constructed and plane mirrors, 3 mm wide, were ground and polished, parallel to the beaker axis, on the outer surface. The behaviour of the film on the three areas A, B and C could then be studied by reflecting plane polarized light from them as in the determinations of film thickness (§ 3). When the inner liquid helium level was in the A region and the bath level in the C region, a film of the appropriate thickness was observed on area A. In addition to the film bright specks corresponding to drops of liquid were seen at B. These drops were 0.1–0.3 mm diameter and

Fig. 15



Conical beaker to show formation of bulk liquid from film,  
Ham and Jackson.

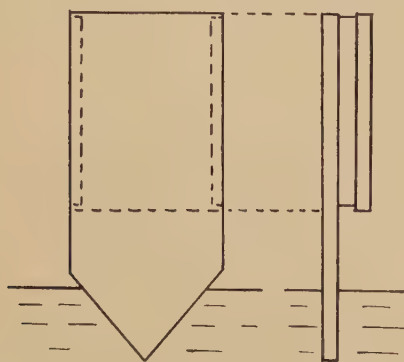
moved downwards at rates of 1–2 cm/sec. Area C showed only the presence of the film, so that the drops had been re-absorbed into it when it flowed over the larger perimeter at C.

The experiments of Ham and Jackson were made with the conical beaker shown in fig. 15, on the outside of which a strip of plane mirror had again been ground and polished. The perimeter of the outside of the relatively thick-walled beaker was approximately equal at the position indicated (halfway along the length) to the inner perimeter at the rim of the beaker. It would therefore have been expected that the upper half of the mirror would initially show the presence of film only and that drop formation would be visible on the lower half. As the beaker emptied by transfer to the outer bath the area of drop formation would descend

towards the bath level and no drops would be visible when the beaker was half full. This proved to be the case, the visible picture giving a very clear impression of the drops of liquid being extruded from the film. The diameters of the drops were in the range 0.1 to 0.5 mm and their velocities up to 2 cm/sec. The drops behaved in the way predicted by Frenkel (1948) for drops which wet the substrate and fall down a vertical surface. He showed that the drops should leave a trail of liquid behind them and only those, whose undeformed radius is larger than  $(3\sigma/\pi\rho g)^{1/2}$ , should move ( $\sigma$ =surface tension,  $\rho$ =density of liquid). Both these features were observed. It may be mentioned that this drop formation was only observed when the substrate was 'clean'. If the surface was contaminated by condensed impurities one only observed a stream of uneven thickness flowing over an irregular substrate.

A further case of the formation of drops of bulk liquid associated with film flow was observed by Jackson and Henshaw (1950). A cylindrical

Fig. 16



Formation of bulk liquid, Lane and Dyba.

beaker of stainless steel, on the outside of which a longitudinal strip of mirror had been polished, was used for the simultaneous measurement of film thickness and transfer rate (see § 8). It was noticed that when the inner liquid helium level was within 0.3 cm of the rim during emptying there was a higher transfer rate than when the inner level was lower and that during this initial period, drops were observed on the mirror surface. Their number decreased as the inner level fell and finally disappeared when the transfer rate had attained its 'normal' value. The observation strongly suggested that the drops were excess liquid which could not be carried by the film though the origin of this excess was not discussed (see, however, § 6).

These observations are all in agreement with the view that the drops have the 'composition' and the properties of bulk liquid helium and are



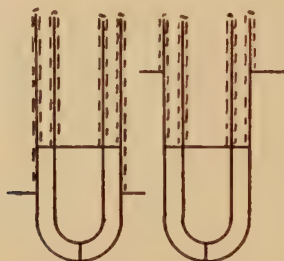
formed from the moving superfluid. As the process is isothermal heat must be supplied when the drops form and removed when they re-enter the film.

Lane and Dyba (1953), Dyba, Lane and Blakewood (1954) have also recorded the formation of bulk liquid from the film during studies of the capillarity of liquid helium II. Two optically flat glass plates were kept apart by thin separators. When the longer plate was immersed in liquid helium II but not the shorter one (fig. 16) it was found that the film was able to fill the gap between the plates with bulk liquid up to the surface tension rise height above the bath level. This was observed even for a gap as large as 75 microns. The later work of McCrum (1954) with an interferometer arrangement of the plates made it clear that the filling of the gap by bulk liquid happens if the gap is bridged at some place below the surface tension rise height by dust particles, hairs or the like minute objects but not if the gap is completely free from them.

### § 11. THE DOUBLE BEAKER EXPERIMENT

If film flow at sub-critical velocities is really the frictionless flow of superfluid, there is a close analogy between such flow and the flow of a

Fig. 17



Double beaker, Daunt and Mendelssohn.

current smaller than the critical current through a superconductor. In the latter case if a circuit is made up of a battery, a superconductor and an ordinary resistor of such a value as to make the current flowing less than the critical current of the superconductor, then no potential difference will be observed across the superconductor. An analogous observation with helium film flow would be to show that such flow, provided it is sub-critical could take place without any difference of level between two quantities of liquid helium II connected by the film.

Such an experiment was carried out by Daunt and Mendelssohn (1946 a) and repeated with certain refinements by Chandrasekhar and Mendelssohn (1955). A glass beaker mounted inside a larger one was partially immersed in liquid helium II, fig. 17 (a) and (b). Figure 18 shows the later form of the double beaker, the upper part consisting of two coaxial glass tubes

sealed to a lower part of copper to ensure the greatest possible temperature uniformity in the system. In each case the inner and outer levels remained together as the double beaker filled or emptied until ultimately the levels coincided with the bath level. In the second experiment the levels remained together within 0.02 cm, the uncertainty of the observation.

Let  $a$  be the radius of the inner beaker and  $b$  that of the outer beaker,  $x$  and  $y$  the heights of the two liquid levels,  $v_1$  and  $v_2$  the mean film velocities along the walls of the inner and outer beakers respectively, then if  $d$  is the thickness of the film the velocities of the levels  $\dot{x}$  and  $\dot{y}$  are given by

$$\begin{aligned}\pi a^2 \dot{x} &= \rho_s 2\pi d a v_1 \\ \pi (b^2 - a^2) \dot{y} &= \rho_s 2\pi d (b v_2 - a v_1).\end{aligned}$$

Fig. 18



Double beaker, Chandrasekhar and Mendelssohn.

Since the observed result is  $\dot{x} = \dot{y}$ , the film velocities are related by

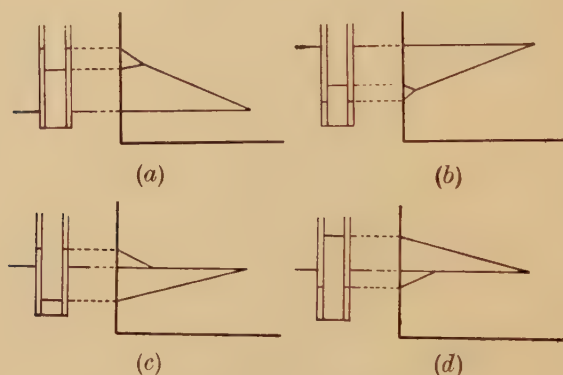
$$v_2 = \frac{b}{a} \cdot v_1.$$

Thus since  $b > a$  the film flow is faster over the outer beaker and since we must suppose this to be the critical velocity, the flow over the inner beaker takes place at a sub-critical velocity. This is therefore one very direct piece of evidence that when the superfluid moves at sub-critical velocities it experiences no frictional resistance, in exact analogy with a superconductor. However, just as in the case of superconductivity, zero resistance alone is inadequate to explain the phenomenon, so with film flow a limiting value of the flow has to be introduced to avoid the flow tending to infinity as the viscosity of the helium tends to zero. This limiting flow is the observed critical transfer rate,

The fact that, within the limits of observation no pressure difference is required to maintain the flow between the inner and outer beaker means that the mean kinetic energy  $\frac{1}{2}\rho_s v_s^2$  of the helium film is not dissipated at the point of entry of the film into the bulk liquid but is completely conserved as free energy. It can be concluded that we have a case of pure reversible potential flow.

In addition to the two cases where the film flow is induced by moving the beaker up or down relative to the bath level with the inner and outer levels initially together, Chandrasekhar and Mendelssohn (1955) have recorded observations when the inner, outer and bath levels are initially all at different heights. The results are shown in fig. 19, where the bath level is assumed to remain at a constant height. It will be seen that in fig. 19(a) and (b), the inner and outer levels soon coalesce and then continue to move together as in the original experiment. Figure 19(c)

Fig. 19



Observations with double beaker.

and (d) are especially interesting as the outer beaker is initially emptying (c) or filling (d) from both the bath and the inner beaker. Then the outer and bath levels remain constant and the sub-critical flow takes place over the outer beaker as shown below. The initial flows when the levels are all different are given by

$$\dot{x} = 2R_c/a$$

$$\dot{y} = 2R_c/(b \pm a)$$

where  $R_c$  = transfer rate.

For the cases c and d when the outer and bath levels have coincided we have the following expression for the velocity of film flow,  $v_2$ , over the outer beaker.

$$\dot{x} = \rho_s 2\pi d a v_1$$

$$\dot{y} = 0$$

giving  $v_2 = a/b \cdot v_1$ .

So with  $v_1$  equal to the critical velocity,  $v_2$  is sub-critical on the outer beaker,



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